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ERRATA

Page 206: Equation 4 should read

$$r_0 \doteq 0.833(V_c)^{1/3}$$

Page 210, table 3: c' should be replaced by k' to agree with equation 12.

Page 224: In equations 29 and 30 substitute "$(273.16p/T)$" for "$(273.16P/T)$".

Page 225: The sentence beginning in line 5 should read:

If U_i is the average velocity of molecules of the ith species relative to U, the mass average velocity of the gaseous mixture, then rigorously (in the absence of thermal gradients, pressure gradients, and external forces):

$$U_i = (n^2/\rho n_i) \sum_{k \neq i}^{f} M_k \, d_{ik} \operatorname{grad} x_k \tag{38}$$

where

$$n = \sum_{k=1}^{f} n_k = p/(RT) \tag{39}$$

is the total number of moles of gas in a cubic centimer and ρ is the overall density of the gas in grams per cubic centimeter.

Page 225: In equation 40 substitute "M_2" for "m_2".

In equation 41 substitute "M_k" for "m_k" and "M_i" for "m_i".

In equation 43 substitute "M_3" for "m_3" and "M_2" for "m_2".

Page 227: Equation 49 should read:

$$Q_3 = \Bigg\{ 3(M_1 - M_2)^2(5 - 4B) + 4AM_1M_2(11 - 4B) + \frac{4}{25}\left(\frac{r_1 r_2}{r_{12}^2}\right)^2$$
$$\cdot \left[\frac{(M_1 + M_2)^3}{(M_1 M_2)^{1/2}}\right]\left[\frac{W^{(2)}(2; kT/\epsilon_1)W^{(2)}(2; kT/\epsilon_2)}{\{W^{(1)}(1; kT/\epsilon_{12})\}^2}\right]\Bigg\}$$

Page 227: Equations 50 through 54 should read:

$$S_1 = AM_1 \{[2(M_1 + M_2)^3/M_2]^{1/2} - 4M_2\} - 3M_2(M_2 - M_1) \tag{50}$$

$$S_2 = AM_2\{[2(M_1 + M_2)^3/M_1]^{1/2} - 4M_1\} - 3M_1(M_1 - M_2) \tag{51}$$

$$Q_1 = A[2(M_1 + M_2)/M_2]^{1/2} [6M_2^2 + (5 - 4B)M_1^2 + 8AM_1M_2] \tag{52}$$

$$Q_2 = A[2(M_1 + M_2)/M_1]^{1/2} [6M_1^2 + (5 - 4B)M_2^2 + 8AM_1M_2] \tag{53}$$

$$Q_3 = [4A^2(M_1 + M_2)^3(M_1M_2)^{-1/2} + 3(M_1 - M_2)^2(5 - 4B)$$
$$+ 4AM_1M_2(11 - 4B)] \tag{54}$$

Page 231: In reference 2 substitute "**35**, 784 (1939)" for "**35**, 1 (1939)".

ORGANIC PERACIDS

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CONTENTS

I. INTRODUCTION

Organic peracids are a relatively new class of organic compounds (30, 31, 33, 172, 173, 174, 175, 176, 177, 182, 183, 184, 185, 186, 187, 188, 189, 224, 399) and within the past several decades a large number of publications have appeared which describe their preparation, properties, and use as oxidizing agents for organic compounds. The activity in this field is not unexpected, since for many applications, particularly in the preparation of oxirane compounds and glycols from unsaturated substances (22, 23, 85, 88, 96, 104, 111, 217, 232, 262, 265, 425, 428, 429, 430, 431, 479, 480, 486, 505, 506, 508) (Section III A and tables 1, 2, 3,

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and 4), organic peracids have numerous advantages over classical inorganic oxidizing agents, such as permanganates, dichromates, chlorates, nitric acid, and hypochlorites. In fact, oxidation with organic peracids represents the only efficient way of preparing some long-chain α-glycols and oxirane compounds.

Oxidations with organic peracids are usually conducted in homogeneous solution and often proceed rapidly under mild reaction conditions with a minimum of side reactions and by-product formation, and the oxidation products are readily isolable in a high degree of purity and in high yield. Since many oxidations with aliphatic peracids are conducted in a solution of the corresponding organic acid, and since the peracid is converted to the organic acid as a result of the oxidation, the solvent may be readily recovered in a pure state for re-use, and the oxidation product obtained as a distillation residue for further processing. Furthermore, some of the more important aliphatic peracids, such as performic and peracetic acids, as well as the carboxylic acids corresponding to them, are soluble both in water and in organic media, thereby affording a wide flexibility in the choice of solvent or solvent mixture for the reaction. When the oxidation product is insoluble in water and the peracid and its corresponding acid are soluble, the oxidation product can usually be isolated in a simple manner by pouring the reaction mixture into water and separating the product mechanically.

Oxidations with organic peracids also lend themselves readily to quantitative and kinetic study (74, 75, 86, 87, 89, 98, 111, 114, 115, 116, 119, 122, 124, 249, 302, 333, 345, 346, 357, 487, 499, 500, 501, 545, 580) (Sections IV and V), since unconsumed peracid can be rapidly determined iodimetrically at suitable time intervals. If desired, a correction can be made in the final yield for the small quantity of product lost as a result of the analyses. Thus it is not only possible to obtain valuable kinetic data as well as a desired product from a single experiment, but by plotting the consumption of peracid against time it is also possible to determine the optimum reaction time for a given temperature with a minimum of effort.

In contrast, many of the classical inorganic oxidizing agents are frequently converted to voluminous and difficult-to-handle end products, such as manganese dioxide from potassium permanganate, or complex mixtures of oxidation products are obtained, as is usually the case in nitric acid or hypochlorite oxidations, thereby rendering isolation of the desired products extremely tedious or impossible. In oxidations with inorganic oxidants, the greatest problem is not to effect the oxidation but to isolate the reaction products in a sufficiently pure state for identification. Also, the need for operating in aqueous media seriously limits the usefulness of some inorganic oxidants for organic reactions. Furthermore, the impossibility or difficulty of following the course of the reaction quantitatively often requires that numerous experiments be conducted and that the products be separated and purified in order to determine the important variable of time.

No discussion of organic peracids can be complete without mentioning the important oxidizing agent hydrogen peroxide. This substance, which is available commercially in aqueous solutions containing from about 3 to 90 per cent hydrogen peroxide, is fairly stable, it has a low equivalent weight, and its reduction

product is water. These characteristics make it extremely attractive as an oxidant for organic reactions, but its relatively high price on an active oxygen basis, its immiscibility with many organic compounds, and the unavailability of its active oxygen for preparative purposes have restricted its large-scale use for organic syntheses. Its low equivalent weight, however, compensates for the high price of the active oxygen, especially when high-molecular-weight compounds are to be oxidized, and in recent years several noteworthy attempts have been made to overcome the other disadvantages and make hydrogen peroxide more generally applicable (56a, 352, 353, 354, 355, 356, 358, 364, 365, 366, 532, 533, 534, 535, 546). Perhaps the most satisfactory technique, however, for utilizing the oxidizing capacity of hydrogen peroxide efficiently in organic reactions is to convert the active oxygen to the peracid form. Organic peracids can be readily prepared, usually with little loss of oxygen, by treating organic acids, acyl halides, or acid anhydrides with 25–100 per cent hydrogen peroxide or with inorganic peroxides (21, 22, 33, 91, 97, 122, 123, 172, 181, 182, 183, 184, 185, 186, 188, 189, 205, 211, 212, 215, 216, 217, 233, 236, 239, 240, 241, 242, 271, 301, 360, 362, 398, 448, 449, 450, 452, 486, 495, 525). In many cases the peracid need not be isolated; it is sufficient to dissolve the substance to be oxidized in the organic acid or anhydride and add the hydrogen peroxide (4a, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 24, 35, 45a, 46, 57, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 70, 70a, 71, 120, 121, 125, 154, 155a, 159, 163a, 168, 169, 170, 171, 171a, 193, 196, 199, 202, 204, 222, 223, 223a, 228, 229, 231, 232, 235, 245a, 251, 252, 253, 254, 255, 256, 257, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 274, 297, 298, 300, 331a, 331b, 333a, 336a, 337, 340a, 342, 351, 386, 388, 389, 390a, 393, 395, 400, 403, 404, 405, 406, 412, 418, 421, 422, 423, 424, 434, 443, 457, 460, 461, 463, 477a, 483, 489, 490, 491, 492, 505, 506, 509, 524, 525, 537, 538, 541, 551, 552, 557). As the peracid forms, it is consumed, and since formation of peracid is an equilibrium reaction, peracid will continue to form and be consumed until very little oxidizable substance remains. Under certain conditions, loss of peroxide can be held to a minimum and substantially stoichiometric utilization of the active oxygen can be effected and quantitative yields of product obtained (505, 506). This *in situ* preparation and consumption of peracids is the technique most frequently employed in oxidations involving aliphatic peracids. By operating either in this manner or by isolating the peracid, which is sometimes necessary since the reaction conditions or the peracid being utilized may not be suitable for the *in situ* technique, the remaining disadvantages of hydrogen peroxide appear to be obviated.

II. PREPARATION AND PROPERTIES OF ORGANIC PERACIDS

A. ALIPHATIC PERACIDS

1. Performic acid

Performic acid was apparently first prepared by D'Ans and coworkers (182, 184, 185, 189), who treated approximately 98 per cent hydrogen peroxide with formic acid in the presence of 1 per cent of sulfuric acid as catalyst. The reaction

is reversible, contrary to the opinion of Clover and Richmond (173) regarding peracids in general, and equilibrium is reached within 2 hr. (equation 1).

$$HCO_2H + H_2O_2 \rightleftarrows HCO_3H + H_2O \tag{1}$$
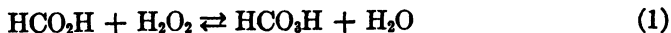
Equilibrium constants for this reaction have been determined by D'Ans and Frey (185) and by Hatcher and Holden (241). Other catalysts that may be employed are nitric, hydrofluoric, and phosphoric acids, and inorganic salts, such as potassium nitrate, ammonium sulfate, sodium bisulfate, sodium phosphite, and barium nitrate. When equimolar proportions of reactants are employed, solutions containing about 48 per cent performic acid are obtained. By employing a 75 per cent excess of hydrogen peroxide and higher proportions of sulfuric acid, and fractionally distilling the equilibrium mixture under vacuum,[2] D'Ans and Kneip (189) obtained solutions containing up to 90 per cent performic acid. Koch and Maisin (301) also prepared performic acid substantially by the procedure of D'Ans, but they employed ether solutions of hydrogen peroxide. Recently Greenspan (233), duplicating the work of D'Ans and Frey (184, 185), employed 90 per cent as well as 30 per cent hydrogen peroxide, and obtained 35.8 per cent and 4.7 per cent solutions of performic acid, respectively. Attainment of equilibrium requires 30 min. when 90 per cent hydrogen peroxide is employed and 2 hr. with the less concentrated hydrogen peroxide. In view of the convenience and greater safety of 30 per cent hydrogen peroxide, as compared with the 90 per cent solution (45), the work of Toennies and Homiller (525) and of Swern and Findley is of interest (507). These investigators employed 30 per cent hydrogen peroxide and extremely large molar excesses (20 or 30:1) of 88–100 per cent formic acid to accelerate attainment of equilibrium, and they demonstrated that equilibrium is reached in less than 1 hr. No catalyst is necessary.

It has also been reported that performic acid is formed when formic acid is treated with oxygen in the presence of unfiltered ultraviolet radiation (164).

Pure performic acid has apparently never been prepared. The 90 per cent solution, however, is a colorless liquid with a characteristic odor. The vapor of performic acid is extremely irritating to the mucous membranes and produces painful inflammations of the skin. It is soluble in water, ethyl alcohol, diethyl ether, chloroform, benzene, and other organic solvents. D'Ans and Kneip (189) have reported that the peracid is more volatile than formic acid. Its solutions are unstable (189, 233, 507, 525), the 90 per cent solution losing 25 per cent of its active oxygen when stored for 24 hr. at 0°C.; the main products of decomposition are carbon dioxide and water (189). At 60° and 80°C. performic acid loses its active oxygen at a very rapid rate, with liberation of carbon dioxide (204). Concentrated solutions of performic acid (60 per cent or higher) can be caused to explode violently by the addition of small quantities of catalysts, such as zinc dust, lead dioxide, red lead, and sodium azide, the first two causing even the 45 per cent strength to explode (189). Numerous other substances cause performic acid solutions to decompose at rates ranging from slow decomposition to detona-

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[2] This is a hazardous procedure, and adequate precautions should be taken to protect the operator.

tion (189). In the absence of catalysts, performic acid explodes when heated rapidly to 80–85°C.

Performic acid reacts rapidly with aqueous solutions of potassium iodide, liberating iodine. This reaction has been employed by Toennies and Homiller for the quantitative determination of performic acid (523a, 525). Performic acid shows typical peroxide properties, such as bleaching dye solutions and reacting with aqueous potassium permanganate.

It has been reported that the incidence of benzopyrene cancer in mice is greatly decreased by one or more injections of 0.1 mg. or less of performic acid (338).

2. Peracetic acid

More work has been published on the preparation of peracetic acid than on that of any other organic peracid. In the first investigations the peracid was not isolated, but was obtained in dilute aqueous solutions by mild hydrolysis of benzoyl acetyl peroxide (221, 399) and diacetyl peroxide (173, 399), by treatment of diacetyl peroxide with alkali followed by acidification (399), and by reaction of diacetyl peroxide or acetic anhydride with dilute hydrogen peroxide solutions (172). A few years later, D'Ans and Friederich (187) treated diacetyl peroxide with concentrated or anhydrous hydrogen peroxide and obtained concentrated solutions of peracetic acid. In a continuation of this work, D'Ans and coworkers treated substantially anhydrous hydrogen peroxide with an equimolar quantity of acetyl chloride (181, 183, 186, 188), acetic acid (182, 184, 185), or acetic anhydride (182, 184, 185, 189). The reaction of acetyl chloride with hydrogen peroxide is better suited for the preparation of acetyl peroxide than peracetic acid, and therefore the last two techniques have completely superseded it for the laboratory preparation of peracetic acid.

When a mixture of equimolar quantities of acetic acid and 98 per cent hydrogen peroxide to which 1 per cent of sulfuric acid has been added is allowed to stand at 14.6°C. until equilibrium is attained (12–16 hr.), a solution containing 50 per cent peracetic acid is obtained (184). When acetic anhydride is employed instead of acetic acid (182, 184, 185), similar results are obtained but in a much shorter time, and when 2 moles of hydrogen peroxide are employed for each mole of acetic anhydride, solutions containing 70 per cent peracetic acid are obtained directly. The equilibrium constants for these reactions have been studied by D'Ans and Frey (185), Hatcher and Holden (241), and Paillard and Briner (397). An excess of acetic anhydride should be avoided to prevent conversion of the peracetic acid to the highly explosive diacetyl peroxide. Vacuum distillation[3] of the 70 per cent solution of peracetic acid yields a fraction, in good yield, containing as much as 90 per cent peracetic acid. Redistillation of fractions containing at least 85 per cent peracetic acid, followed by fractional freezing and centrifuging, yields pure peracetic acid (184).

Although numerous other investigators (21, 22, 91, 97, 205, 217, 233, 236, 240, 241, 448, 449, 450, 452, 486) have studied the reaction of hydrogen peroxide with

[3] See footnote 2.

acetic acid or anhydride, only minor improvements have been made in the original procedures of D'Ans and his colleagues. Thus, Erlenmeyer (205) reported that it is better to add the hydrogen peroxide to the acetic anhydride–sulfuric acid mixture. Böeseken and coworkers (91, 97) claimed that peracetic acid solutions free of diacetyl peroxide can be obtained by treating acetic anhydride with 45–50 per cent hydrogen peroxide and employing p-toluenesulfonic acid as catalyst. They also pointed out that the stability of the peracetic acid solution is improved by vacuum distillation, which should be carried out in the dark. Smit (486) found that 30 per cent hydrogen peroxide can be employed instead of highly concentrated or anhydrous hydrogen peroxide. Grundmann and Trischmann (236) also employed 30 per cent hydrogen peroxide and emphasized that the reaction temperature should not be too low during the addition of the reactants; otherwise complete mixing may occur before any reaction has taken place, at which point the reaction may proceed with explosive violence. Findley, Swern, and Scanlan (217) treated acetic anhydride with 25–30 per cent hydrogen peroxide and found that a catalyst is unnecessary. The reaction temperature employed by these investigators was 40°C., and yields as high as 90 per cent were obtained (503).

Peracetic acid can also be prepared by the direct oxidation of acetaldehyde with oxygen. The Consortium für Elektrochemische Industrie (174, 175, 176) and Galitzenstein and Mugdan (224) demonstrated that peracetic acid is formed when freshly distilled dry acetaldehyde is treated with oxygen at $-10°$ to $-20°C$. in the liquid phase. The oxygen absorption rate is considerably accelerated when the reaction mixture is irradiated with ultraviolet light. Manganese salts and water must be rigorously excluded, but salts of cobalt, chromium, iron, uranium, and vanadium may be employed as catalysts (175, 177, 224, 562). Inert solvents, such as acetic acid or ethyl acetate, may also be employed (309). The unreacted acetaldehyde is removed by distillation at low temperatures, yielding as a residue peracetic acid containing some acetic acid. While unreacted acetaldehyde is present in the mixture, the temperature must not be allowed to rise to room temperature; otherwise a violent oxidation of acetaldehyde to acetic acid occurs, with concomitant destruction of the peracetic acid. Although the oxygen oxidation of liquid acetaldehyde gives fair yields of peracetic acid, Bloomfield and Farmer (72) reported that in a large-scale operation a violent explosion resulted.

Vapor-phase oxidation of acetaldehyde under proper conditions may also be employed to prepare peracetic acid (73, 79, 151, 197a, 243, 391, 392), but such oxidations are employed mainly in the preparation of acetic acid from acetaldehyde. It has been pointed out that not more than 30 per cent of the oxygen theoretically necessary to convert the aldehyde to the peracid should be employed (73, 151).

The direct oxygen oxidation of acetaldehyde under a variety of conditions has been the subject of many investigations (1, 78, 79, 130, 131, 244, 246, 299, 332, 333, 391, 402, 459, 562, 570, 571) in which the kinetics and mechanism of the oxidation, rather than the preparation and isolation of the peracetic acid, were

studied. Peracetic acid is formed as an intermediate during the oxidation of acetaldehyde to acetic acid, and under certain conditions the peracid can be made the main product.

Other procedures for the preparation of peracetic acid consist in the reaction of acetic acid with oxygen in the presence of unfiltered ultraviolet radiation (165), the reaction of acetic acid with ozone (397), the reaction of ketene with hydrogen peroxide (184), the reaction of acetaldehyde with ozone–oxygen mixtures (143, 144, 219), the reaction of aqueous sodium perborate with acetic anhydride (495), and the reaction of boric–acetic anhydride with hydrogen peroxide (184). The last-named reaction produces peracetic acid in 79 per cent yield, whereas the reaction of acetic acid with oxygen or ozone yields only small quantities of peracetic acid. In the reaction of ketene with hydrogen peroxide, the peracetic acid which forms is rapidly converted to diacetyl peroxide by further reaction with ketene. In the reaction of acetaldehyde with ozone–oxygen mixtures, it is the oxygen which converts the aldehyde to the peracid; the ozone serves only as a catalyst (140, 142, 145). Thus, in the reaction of benzaldehyde-oxygen–ozone mixtures, the yield of perbenzoic acid decreases as the oxygen content decreases, and in the absence of oxygen no peracid is formed. The rate of absorption of oxygen by benzaldehyde, however, is increased by the presence of one part of ozone in ten million parts of oxygen (146, 147).

Pure peracetic acid, $d_4^{15°} = 1.226$, is a colorless liquid which melts at 0.1°C. (184). Its boiling point has been reported as 20–30°C. at 10–20 mm. (184), 25°C. at 12 mm. (21), 35–36°C. at 29 mm. (22), and 105°C. (156). It is readily soluble in water, ethyl alcohol, diethyl ether, sulfuric acid, acetic acid, and other organic solvents (156). It has an intensely sharp odor, and it reacts strongly with cork, rubber, and the skin (184). It has bactericidal (312) and bleaching properties (163), in common with other peracids and peroxides in general.

Peracetic acid is reported to be insensitive to impact (156), but it explodes violently when heated at 110°C. (184). The region of explosive decomposition of mixtures of oxygen and peracetic acid has been investigated (1). When peracetic acid is heated at 130°C. in a bomb, it explodes, yielding methane, ethane, ethylene, methyl alcohol, and carbon dioxide, and when heated at 150°C. in an atmosphere of ammonia it is converted to methylamine, methyl alcohol, and oxygen (213). Hatcher and Toole (245) reported that peracetic acid decomposes when heated, forming carbon dioxide, formic acid, and glycolic acid. It is slowly decomposed by platinum black at room temperature, and it is rapidly hydrolyzed to acetic acid and hydrogen peroxide by aqueous sodium hydroxide (119). Manganese salts also catalyze the decomposition of peracetic acid, the products being acetic acid, carbon dioxide, carbon monoxide, and oxygen (333). In the absence of catalysts, concentrated solutions of peracetic acid are fairly stable at room temperature (15°C.), 87–95 per cent solutions remaining virtually unaltered on standing for about 5 weeks (189). In this respect, peracetic acid differs markedly from performic acid, which is unstable. D'Ans and Kneip (189) reported that a 50 per cent solution of peracetic acid shows no loss of peracid after storage for 14 days, and Greenspan (233) reported that a 45 per cent

solution retains 75 per cent of the peracid after 49 days. Solutions stabilized with one hundred parts per million of sodium pyrophosphate contain 94 per cent of the peracid after 49 days' storage (233). Other inorganic and organic stabilizers for peracids have also been suggested (377, 451). Five to ten per cent solutions of peracetic acid in acetic acid, however, show significant oxygen losses at room temperature but very little oxygen loss when stored at 0–5°C. (217).

A 40 per cent solution of peracetic acid in acetic acid is sold commercially (156), and information is available regarding the stability, flammability, pH, flash point, solubility, specific gravity, and conditions for the storage and handling of this solution.

Procedures for the analytical determination of peracetic acid in the presence of hydrogen peroxide and diacetyl peroxide have been described (34, 184, 241, 486).

Ethyl peracetate has been reported (32). This compound cannot be classed as a derivative of peracetic acid and ethyl alcohol, but rather as a derivative of acetic acid and ethyl hydroperoxide (363, 569).

3. Perpropionic acid

Dilute solutions of perpropionic acid have been prepared from propionyl peroxide by mild aqueous hydrolysis (173) or by treatment with aqueous hydrogen peroxide (172), and also by the reaction of propionic acid with 30 per cent hydrogen peroxide (271). Concentrated solutions have been prepared by D'Ans and coworkers (182, 184) by treating propionic acid or its anhydride with approximately 100 per cent hydrogen peroxide. Equilibrium constants for these reactions have been reported by D'Ans and Frey (185). When equimolar proportions of propionic acid and hydrogen peroxide, to which 1 per cent of sulfuric acid has been added as catalyst, are allowed to stand at 14.8°C. for about 12–16 hr., a solution containing about 55 per cent of perpropionic acid is obtained directly. When 1 mole of propionic anhydride is treated with 2 moles of hydrogen peroxide at room temperature (sulfuric acid catalyst) until equilibrium is attained, and the reaction mixture is then distilled under vacuum,[4] fractions containing up to 89 per cent perpropionic acid are isolated in good yield. By fractional freezing and centrifuging, perpropionic acid of 99.5 per cent purity is obtained.

Perpropionic acid has also been prepared from propionaldehyde by oxygen oxidation in the liquid phase at low temperatures (174, 175, 176, 177, 224, 570) in an analogous manner to the preparation of peracetic acid from acetaldehyde. The same catalysts are suitable, and the same precautions must be observed (dry oxygen, absence of manganese salts, etc.). Steacie and coworkers (497) studied the oxygen oxidation of propionaldehyde at 120–170°C. and reported that perpropionic acid is formed as an intermediate, although it was not isolated. Newitt and coworkers (391, 392) also studied the vapor-phase oxidation of propionaldehyde and reported that aqueous solutions of the oxidation products contain perpropionic acid, as well as a peroxide isomeric with it. Recently it has been shown that peracids, including perpropionic acid, can be obtained by the vapor-phase oxidation of aldehydes, provided that not more than 30 per cent of

[4] See footnote 2.

the oxygen theoretically necessary to convert the aldehyde to the peracid is employed (73, 151).

Perpropionic acid can also be prepared by treating propionaldehyde in hexane or carbon tetrachloride solution with ozone–oxygen mixtures (143).

When propionic acid is treated with oxygen in the presence of unfiltered ultraviolet radiation, the peracid is formed (165). Its rate of formation under these conditions is much greater than that of peracetic acid when acetic acid is similarly treated.

Pure perpropionic acid has also been prepared in good yield by treating boric-propionic anhydride with hydrogen peroxide (184).

Perpropionic acid is analogous to peracetic acid in its physical and chemical properties. Its melting point is −13.5°C. (184). It is more stable and less explosive than peracetic and performic acids, and on heating it deflagrates (184, 212). When heated in a steel autoclave it is converted to carbon dioxide, ethylene, ethane, and methane; at moderate temperatures it is converted to ethyl alcohol and carbon dioxide (212).

4. Perbutyric acid

Perbutyric acid has been prepared by the reaction of butyric acid or butyric anhydride with hydrogen peroxide (182, 184, 271). Equilibrium constants for these reactions have been reported by D'Ans and Frey (185). By vacuum distillation,[5] followed by fractional freezing and centrifuging, 95.4 per cent perbutyric acid has been obtained (184).

Perbutyric acid has also been prepared by the reaction of butyraldehyde with ozone–oxygen mixtures (143, 145, 148, 149, 150, 219), by the oxygen oxidation of butyraldehyde (391, 392), by the electrochemical oxidation of butyl alcohol (440), by the oxygen oxidation of butyric acid in the presence of filtered or unfiltered ultraviolet radiation (165), and by the reaction of boric–butyric anhydride with hydrogen peroxide (184).

Perbutyric acid is similar to the other peracids discussed, except that it is more stable and it deflagrates with less force than perpropionic acid, with partial carbonization (184). The pure compound has not been reported, but the mixture containing 95.4 per cent perbutyric acid melts at −10.5°C. (184) and a product containing 71.8 per cent boils at 26–30°C. at 12 mm. (219). When heated at 150°C. in a steel bomb perbutyric acid explodes, yielding much methane, carbon dioxide, carbon monoxide, and carbon, and a little propylene (214).

5. Miscellaneous

The remaining aliphatic peracids described have been studied to a limited extent, and in most cases only their method of preparation has been reported.

Perisovaleric acid, b.p. 31–32°C. at 1 mm., and perheptanoic acid have been prepared by the reaction of the corresponding aldehydes in carbon tetrachloride solution with ozone–oxygen mixtures (219). Perisovaleric acid has also been

[5] See footnote 2.

prepared by treating isovaleric acid with oxygen in unfiltered ultraviolet radiation (165).

Percaproic acid (m.p. 15°C.; b.p. 61–62°C. at 13 mm. and 41–42°C. at 0.5 mm.) has been prepared by the reaction of caproic anhydride with 93 per cent hydrogen peroxide (216). It has also been prepared by the reaction of caproic acid with 30 per cent hydrogen peroxide (271). Percaproic acid is apparently formed as an intermediate in the electrolysis of caproic acid and potassium caproate, but under these conditions it decomposes to carbon dioxide and amyl alcohol (210, 216). Percaproic acid is readily soluble in ethyl alcohol, diethyl ether, and petroleum ether, and slightly soluble in water. It decomposes slowly on storage at room temperature, and on rapid heating it detonates and ignites. On heating in a metal pipe at 240°C. it yields 1-pentene, n-caproic acid, n-amyl caproate, and carbon dioxide. It displays typical peracid properties, rapidly liberating iodine from potassium iodide and imparting a yellow color to titanium sulfate solution, and it is rapidly decomposed by concentrated potassium hydroxide (216).

Percrotonic acid has been prepared in dilute aqueous solution by the mild hydrolysis of crotonyl peroxide (173). Solutions containing 50 per cent percrotonic acid have been prepared by the reaction of crotonic anhydride with 94 per cent hydrogen peroxide (215). Attempts to obtain the pure peracid by distillation have been unsuccessful because of its instability. On being heated rapidly in a steel bomb percrotonic acid explodes, yielding carbon dioxide, unsaturated hydrocarbons, crotonic acid, and resins (215).

D'Ans and Frey (184) have reported that they detected perpalmitic acid, but no details were given. They presumably prepared this peracid by the reaction of palmitic acid with concentrated hydrogen peroxide.

Pertrichloroacetic acid has been prepared by the reaction of trichloroacetic anhydride with pure hydrogen peroxide (211), but the peracid is extremely unstable, being rapidly converted to phosgene, hydrogen chloride, carbon dioxide, and chlorine. Permonochloroacetic acid has been similarly prepared and can be distilled. It boils at 33–34°C. at 3.5–4 mm. (182, 398). Permonochloropropionic, perdichloropropionic, perbromopropionic, permonochloroacetic, perdichloroacetic, and perbromoacetic acids have been mentioned in a patent but no preparative details were given (268).

Perlactic, perglycolic, perpyruvic, and permesoxalic acids have been reported as intermediates in the oxidation of the corresponding aliphatic acids with hydrogen peroxide (238, 241, 245). Perlauric acid has been mentioned in a recent paper (485) but a description of its preparation or properties was not reported.

Long-chain persulfonates of unknown structure have been prepared by treating stearic acid with chlorosulfonic acid, followed by reaction of the resulting sulfonyl chloride with sodium peroxide (192, 336).

Hatcher and Holden (239, 241) have reported that peroxalic acid is not formed when oxalic acid is treated with dilute aqueous hydrogen peroxide. Koch and Maisin (301), however, have indicated that this peracid can be obtained from oxalic acid and hydrogen peroxide by the procedure of D'Ans and Kneip (189),

but no details were given. Milas and Panagiotakos (362) prepared diperoxalic acid by treating a pyridine–ether solution of hydrogen peroxide with oxalyl chloride at −20°C. This peracid is reported to be a powerful oxidizing agent, but no additional information regarding its properties could be found.

Monopersuccinic acid, m.p. 107°C. (with decomposition), has been prepared by the mild aqueous hydrolysis of β-carboxypropionylperoxide (172). It is purified by crystallization from a mixture of chloroform and ether. It is more soluble in water than is succinic acid, and it is also soluble in alcohol, acetone, and ethyl acetate. This peracid is relatively stable, and on being heated it liberates approximately 1 mole of carbon dioxide per mole of peracid (172). Dilute aqueous solutions of this peracid have been obtained by treating succinic anhydride with dilute aqueous solutions of hydrogen peroxide or persalts, such as sodium peroxide or sodium perborate (448, 449, 450, 452).

The preparation of dilute solutions of other aliphatic peracids, such as permaleic, perglycolic, and perglutaric acids, by the reaction of the corresponding acid anhydride with a dilute solution of an inorganic peroxide, has been mentioned in several patents (448, 449, 450, 452).

Tertiary butyl peresters of stearic, undecylenic, crotonic, succinic, and adipic acids have been prepared in good yields by treating tertiary butyl hydroperoxide with the appropriate acid chloride (363) but, as discussed earlier, these products are properly classified as derivatives of tertiary butyl hydroperoxide and organic acids rather than as derivatives of organic peracids.

B. AROMATIC AND CYCLIC PERACIDS

1. Perbenzoic acid

Perbenzoic acid was apparently isolated for the first time by Baeyer and Villiger (30, 31), who treated benzoyl peroxide with sodium ethoxide in ether–alcohol solution, followed by acidification. Subsequent investigators have had difficulty in obtaining good yields by their technique, however, and numerous modifications and improvements have been introduced. Levy and Lagrave (317) and Tiffeneau (513) carried out the reaction in toluene solution and reported 80–93 per cent yields. Hibbert and Burt (258), who studied the numerous experimental variables involved, pointed out that the order of addition of the reactants is important. They obtained 90 per cent yields. Braun (138) employed methyl alcohol–chloroform mixture as the solvent and sodium methoxide as the base and reported 82–86 per cent yields. Kleinschmidt and Cope (299a) employed methylene chloride instead of chloroform to extract the perbenzoic acid, and Harris and Smith (237) employed ligroin. Brooks and Brooks (153) and Bergmann and Witte (55) treated benzoyl chloride with aqueous sodium peroxide at low temperatures and reported yields of perbenzoic acid of 91 and 80 per cent, respectively. Wieland and coworkers (564) employed benzene–ethyl alcohol mixtures and reported 80–90 per cent yields. Isii (271) treated benzoic acid with hydrogen peroxide and reported the formation of perbenzoic acid, but he did not give details and yields. Calderwood and Lane (161) employed carefully washed chloroform and an excess of sulfuric acid. Rochen (462) employed benzoyl peroxide and

aqueous sodium peroxide or alcoholic sodium hydroxide, and obtained 50–55 per cent and 60–90 per cent yields, respectively. Kolthoff, Lee, and Mairs (303) reported that Braun's procedure (138) was the best for preparing perbenzoic acid but introduced the following modifications: (a) The reaction mixture was maintained below 0°C. during the addition of the chloroform solution of benzoyl peroxide, (b) the solution was extracted immediately after the addition was complete, (c) water was added before transferring the solutions to the separatory funnel, (d) carbon tetrachloride was used for washing instead of chloroform, (e) any emulsion was discarded, (f) after acidification, benzene rather than chloroform was employed for extraction, and (g) the benzene solution was stored in the dark at about 10°C.

Perbenzoic acid can also be prepared by the oxygen oxidation of benzaldehyde under controlled conditions. The oxygen oxidation of benzaldehyde to yield benzoic acid has been studied since the early part of the nineteenth century (579), but only comparatively recent investigators (31, 80, 221, 350, 563) have suggested that perbenzoic acid is an intermediate in this reaction, although the peracid was not isolated. Jorissen and van der Beek (279, 280, 281, 542), however, were apparently the first workers to isolate perbenzoic acid from such a system. They treated benzaldehyde, dissolved in a series of solvents, with oxygen while exposing the solutions to sunlight, and they reported that, in acetone solution, they obtained a 63 per cent yield of percompound. On evaporation of the solvent and vacuum distillation of the residue, perbenzoic acid was isolated. Acetone was by far the best solvent and carbon tetrachloride was moderately satisfactory. Jorissen and van der Beek prepared relatively small quantities of perbenzoic acid by this technique. Swern, Findley, and Scanlan (508) re-investigated this reaction and demonstrated that the reaction can be considerably accelerated by employing ultraviolet radiation instead of sunlight, and they prepared perbenzoic acid in 40 per cent yields on a fairly large laboratory scale. p-Bromobenzaldehyde, p-chlorobenzaldehyde, and m-chlorobenzaldehyde, however, yield little or no peracid when similarly treated (543).

The mechanism and kinetics of the reaction of oxygen with benzaldehyde, as well as conditions for accelerating and inhibiting the oxidation, have been studied by numerous workers (3, 26, 27, 28, 29, 77, 134, 155, 177a, 177b, 278, 281, 310, 349, 367, 444, 445, 446, 447, 455, 511, 531, 561, 562, 570, 571, 575, 576, 577, 578). Of interest is the observation of Wieland (561, 562, 571) that benzaldehyde autoxidizes at the same rate in the presence or absence of water, yielding perbenzoic acid, whereas in the autoxidation of acetaldehyde water must be excluded in order to obtain peracetic acid. Several investigators have pointed out that rigorously purified benzaldehyde does not autoxidize in the dark (310, 444, 445) and that the oxidation is retarded by infrared radiation (531). Some important inhibitors of this oxidation are iodine, hydroquinone, diphenylamine, and sulfur (367), pumice stone, Florida earth, and blood charcoal (155), lead tetraethyl, anthracene, phenol, and trichloroacetic acid (26), hydrocyanic acid and pyrophosphoric acid (310), catechol and resorcinol (77), and sulfur (278). The reaction is accelerated by sunlight (279, 280, 542), ultraviolet radiation (27, 444, 447, 508,

531), numerous metallic salts, notably those of manganese, iron, copper, silver, and nickel (310, 444, 446), and iron powder (542).

Perbenzoic acid can also be prepared by the reaction of benzaldehyde with ozone–oxygen mixtures (140, 141, 142, 144, 146, 147, 148, 149, 150, 219), by the reaction of benzoic acid with ozone (142), by the mild aqueous hydrolysis of benzoyl acetyl peroxide (173, 221), by the reaction of benzoyl acetyl peroxide with sodium ethylate (221), and by the reaction of benzoic anhydride with alkaline aqueous solutions of persalts or hydrogen peroxide (173, 448, 449, 450, 452).

Tertiary butyl perbenzoate (363) and trans-9-decalyl perbenzoate (178) have been prepared by the reaction of benzoyl chloride with tertiary butyl hydroperoxide and trans-9-decalin hydroperoxide, respectively.

Perbenzoic acid is a white crystalline solid, which can be crystallized from chloroform–ethanol mixtures (335) or from petroleum ether (31). It melts at about 41°C. (31, 219), and may be distilled under vacuum with partial decomposition. A boiling range of 97–110°C. at 13–15 mm. pressure has been reported (31). It is soluble in most common organic solvents, and slightly soluble in water. It may be sublimed, and it is somewhat volatile with steam. It has a strong, unpleasant odor, similar to that of hypochlorous acid.

Perbenzoic acid displays typical peracid oxidizing properties, liberating iodine rapidly from potassium iodide, decolorizing indigo, and oxidizing ferrous and manganese salts. The sodium, potassium, ammonium, and barium salts have been prepared and studied by Baeyer and Villiger (31). Other salts, such as the calcium, silver, and strontium salts, are too unstable to be isolated and purified (31). The barium salt, which is only slightly soluble in water, has been employed in the purification of perbenzoic acid (31). Perbenzoic acid yields benzoyl peroxide when treated with benzoyl chloride, and benzoyl acetyl peroxide when treated with acetic anhydride (31).

Perbenzoic acid is stable at room temperature, but it decomposes smoothly into benzoic acid, with the evolution of gases containing oxygen, when it is heated at 80–100°C. (31). It does not explode when struck but when heated in a steel bomb it detonates, yielding benzoic acid, oxygen, and traces of carbon dioxide (206). It has been reported to be stable in the presence of manganese dioxide, platinum, or silver (31), but recently Berezovskaya and Semikhatova (47) reported that the first two compounds catalyze its decomposition.

The stability of perbenzoic acid and of its sodium salt has been studied by many investigators (47, 89, 153, 161, 227, 303, 349, 357, 429, 511). Prileschajew (429) studied the kinetics of the decomposition of perbenzoic acid in chloroform, ether, and carbon tetrachloride solution. Böeseken and Blumberger (89) reported that perbenzoic acid is stable in chloroform above 30°C. Gelarie and Greenbaum (227) reported that at room temperature aqueous solutions of sodium perbenzoate evolve oxygen rapidly, yielding sodium benzoate in solution. The decomposition is accelerated by impurities, but even the pure compound in water is 95 per cent decomposed in 24 hr. Brooks and Brooks (153), however, showed that at 0°C. sodium perbenzoate is stable in the presence or absence of excess alkali. Meyer (349) reported that perbenzoic acid is stable at 0°C. in chloroform solution con-

taining benzaldehyde or acetate hemin but less stable when both benzaldehyde and alkali are present. He also showed that the peracid rapidly disappears in the presence of acids, phosphates, pyridine, or pyridine hemin. Berezovskaya and Semikhatova (47) demonstrated that the decomposition of perbenzoic acid in diethyl ether solution is catalyzed by platinum and that the presence of ethyl alcohol in the ether solution inhibits the reaction. Calderwood and Lane (161) showed that perbenzoic acid in unwashed chloroform at 6°C. begins to decompose within 1 to 2 weeks, whereas solutions in washed chloroform are perfectly stable for about two months. Kolthoff, Lee, and Mairs (303), however, have recommended that the use of chloroform as a solvent for perbenzoic acid be discouraged, since the peracid catalyzes the decomposition of the solvent by oxygen. Chloroform containing about 10 per cent of benzene is satisfactory.

Aqueous solutions of perbenzoic acid are reported to be germicidal (221). Perbenzoic acid can be employed for the vulcanization of rubber (396).

2. Miscellaneous

Monoperphthalic acid was first reported by Baeyer and Villiger (33), who prepared this compound by treating finely divided phthalic anhydride with an alkaline solution of dilute aqueous hydrogen peroxide, followed by acidification. Yields were not reported. They also prepared this peracid by hydrolyzing phthalyl peroxide with the calculated quantity of ice-cold sodium hydroxide solution, but no details of this method were given (33). The former reaction has been reinvestigated by Böhme (122, 123), who employed 30 per cent hydrogen peroxide and reported 65–70 per cent yields of monoperphthalic acid. Monoperphthalic acid has also been prepared by the reaction of phthalic anhydride with aqueous sodium perborate (448, 449, 450, 452, 495) and also with aqueous sodium peroxide (448, 449, 450, 452). Bachmann and Cooper (25) have reported that it is advantageous to employ 40 per cent sodium hydroxide and to add crushed ice to the reaction mixture when Böhme's method is employed.

Monoperphthalic acid is a white crystalline solid which softens at 110°C. and is converted to phthalic acid, with the evolution of gas (33). It is soluble in water and diethyl ether, and only slightly soluble in chloroform and benzene. It shows typical peracid oxidizing properties and is converted to hydrogen peroxide and phthalic acid on aqueous hydrolysis (33, 173).

Monoperphthalic acid is more stable than perbenzoic acid (33, 167), solutions of the former losing less than 10 per cent of their active oxygen content in 30 days at 0°C. and about 20 per cent at 12–14°C. (33). When chloroform is employed as a solvent, it should be freshly distilled before use (167).

In common with other organic peracids, monoperphthalic acid is reported to have a germicidal effect (221).

Tertiary butyl diperphthalate has been prepared by the reaction of phthalyl chloride with tertiary butyl hydroperoxide (363).

Diperterephthalic acid was also prepared by Baeyer and Villiger (33) by the reaction of terephthalyl chloride in ether solution with an alkaline solution of hydrogen peroxide. The free acid is a white crystalline solid, slightly soluble

in water, which explodes when heated or struck. It is readily converted to terephthalic acid by reducing agents and it is similar to perbenzoic acid in reactivity.

Dimethyl, diethyl, dipropyl, and diisopropyl perterephthalates have been prepared from terephthalyl chloride and the barium salt of the corresponding hydroperoxides (32, 343, 458).

Percinnamic acid has been prepared in 80 per cent yield by Bodendorf (76) by the reaction of cinnamyl peroxide with sodium ethylate in ethyl alcohol–chloroform solution. It melts at 67–68°C. (with decomposition), and it is relatively stable. In benzene solution at room temperature it remains unchanged for days, and when the solution is maintained at 50°C. for 24 hr., only 12 per cent of the active oxygen is lost.

p-Methoxyperbenzoic, p- and m-nitroperbenzoic, α- and β-pernaphthoic, and phenylperacetic acids have been prepared from the corresponding diacyl peroxide and sodium ethylate (345).

Although Baeyer and Villeger (33) stated that Brodie (152) may have obtained the barium salt of percamphoric acid in 1864, the free acid was first isolated and characterized by Milas and McAlevy (359), who treated d-camphoric anhydride with an aqueous solution of sodium peroxide. The peracid is a white solid which melts at 49–50°C., and is soluble in water and nearly all organic solvents. It is hydrolyzed in aqueous solution to camphoric acid and hydrogen peroxide. Percamphoric acid is more stable than perbenzoic acid (357). It is stable for weeks at 0°C. in the absence of moisture, and at room temperature it decomposes slowly to camphoric acid and oxygen. When heated at 80–100°C. it decomposes explosively.

The secondary methyl perester tertiary methyl camphorate has been prepared by the reaction of the barium salt of methyl hydroperoxide with tertiary methyl ester secondary camphoryl chloride (359).

Perfuroic acid has been prepared by Milas and McAlevy (360) by the reaction of difuroyl peroxide with sodium methoxide in diethyl ether–methyl alcohol solution. This peracid is probably obtained in small quantity during the autoxidation of furfural at 0°C. in petroleum ether, but it is not isolable from such a system (360). The preparation of dilute solutions of this peracid by the reaction of furoic anhydride with alkaline solutions of inorganic peroxides has been described in patents (448, 449, 450, 452). Perfuroic acid is a crystalline compound, melting at 59.5°C. (with decomposition), which can be recrystallized from carbon tetrachloride. Perfuroic acid is extremely soluble in water, and on standing hydrolyzes to furoic acid and hydrogen peroxide. It is insoluble in petroleum ether and soluble in most of the other common organic solvents. At 0°C. in chloroform solution, as well as in the absence of solvent, perfuroic acid is fairly stable, but at 30–40°C. it decomposes with explosive violence, yielding furoic acid, carbon dioxide, an alkali-soluble resin, and small amounts of 4,5-epoxyfuroic acid (361). At room temperature, decomposition of the peracid ranging from moderate to violent explosions may be caused by the addition of small quantities of organic and inorganic solids, such as animal charcoal and barium, calcium, strontium,

copper, and magnesium chlorides (361). Exposure of the solid acid or its acetic acid solution to ultraviolet light of wave lengths ranging from 4500 to 3600 Å. causes rapid decomposition. In chloroform solution at 35° and 40°C., the decomposition is monomolecular (361).

Tertiary butyl perfuroate has been prepared by the reaction of furoyl chloride with tertiary butyl hydroperoxide (363).
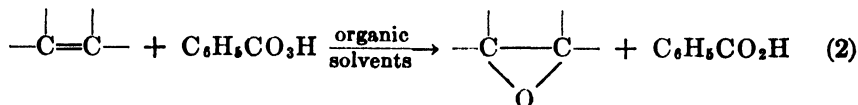
Several aromatic sulfur-containing peracids have been reported. Willstätter and Hauenstein (573) prepared a solution of benzoyl monopersulfuric acid by the reaction of monopersulfuric acid with benzoyl chloride at 0°C. The free acid cannot be isolated but the potassium salt, melting at 50–55°C., can be. The salt is soluble in water and detonates when ground or when heated at 70–80°C. When shaken with sulfuric acid, it is cleaved to perbenzoic and sulfuric acids, whereas on treatment with aqueous alkali it is converted to benzoic and monopersulfuric acids. Salts of p-toluenepersulfonic, β-naphthalenepersulfonic, and amylnaphthalenepersulfonic acids have been prepared from sodium, calcium, or silver peroxide and the corresponding arylsulfonyl chlorides (192, 336). Other related persulfonic acids have been prepared by the reaction of peroxides of the types $RSO_2O_2SO_2R$ and $RSO_2O_2SO_2R'$ with peroxides (336), and also by the reaction of metallic salts of organic sulfonic acids with hydrogen peroxide and aqueous sodium peroxide (336). A complex persulfuric acid has been prepared by treating o-phenanthrolene with silver salts and ammonium persulfate (336).

III. ORGANIC PERACIDS AS OXIDIZING AGENTS

A. OXIDATION OF UNSATURATED COMPOUNDS

1. Preparation of oxirane (α-epoxy) compounds

The preparation of oxirane compounds by the reaction of unsaturated substances with an organic peracid was discovered by the Russian chemist Prileschajew (425, 428, 429, 430, 431), who demonstrated that perbenzoic acid is an efficient oxidizing agent for this reaction and that the reaction is a general one for the epoxidation of compounds with isolated double bonds. The reaction proceeds as shown in equation 2.

$$-\overset{|}{C}=\overset{|}{C}- \; + \; C_6H_5CO_3H \; \xrightarrow[\text{solvents}]{\text{organic}} \; -\overset{|}{C}\underset{\diagdown_O\diagup}{\quad}\overset{|}{C}- \; + \; C_6H_5CO_2H \qquad (2)$$

Although considerable evidence has been collected that the reaction proceeds as shown in the equation, some workers (376, 511) have suggested that the peracid adds directly to the double bond, followed by splitting out of benzoic acid. This erroneous idea has found its way into a standard reference work on organic chemistry (2).

This epoxidation reaction, which is an excellent one for preparative purposes, proceeds under mild reaction conditions and is conducted in a convenient organic solvent, such as chloroform, ether, acetone, and dioxane. The reaction time varies considerably and depends to a great extent on the number and nature of the groups attached to the unsaturated linkage (501) (discussed in greater detail in

Section V). In many of the epoxidations, quantitative yields of oxirane compounds are obtained, yields above 75 per cent usually being obtained. The reaction is especially valuable for the epoxidation of non-volatile, water-insoluble, unsaturated compounds, which usually cannot be satisfactorily converted to the oxirane compound either by way of the chlorohydrin or by direct oxidation with oxygen. Epoxidation with perbenzoic acid has been used in the preparation of oxirane compounds from a large number of unsaturated substances, which are listed alphabetically in table 1.

Since perbenzoic acid can be conveniently and readily prepared by the oxygen oxidation of benzaldehyde (279, 280, 281, 508, 542), several groups of investigators have treated solutions of benzaldehyde and an unsaturated compound with air or oxygen. The perbenzoic acid is consumed as it is formed. This application of the perbenzoic acid epoxidation technique, in which the isolation of the peracid is avoided, has been applied to the oxidation of octenes (407), oleic acid (447, 508), stilbene (447), styrene (447) and squalene (447); in general, good yields of oxirane compounds are obtained.

Monoperphthalic acid has also been employed to convert unsaturated compounds to the corresponding oxirane compounds, but this reaction has not been studied so extensively as epoxidation with perbenzoic acid. Although Böhme (122, 124) was apparently the first to demonstrate that monoperphthalic acid is consumed by reaction with double bonds, Chakravorty and Levin (167) were the fi st investigators actually to isolate oxirane compounds by the oxidation of unsaturated compounds with this oxidizing agent. The epoxidation reaction is conducted under the same conditions as that with perbenzoic acid, and good yields of oxirane compounds are usually obtained. Epoxidation with monoperphthalic acid has been applied most extensively to naturally occurring products such as sterols and polyenes. Unsaturated substances which have been converted to oxirane compounds by oxidation with monoperphthalic acid are listed alphabetically in table 2.

For a long time it was assumed that oxirane compounds could not be prepared by the epoxidation of olefins with peracetic acid, since the products usually isolated from such reactions were α-glycols or hydroxyacetates (see later discussion). Böeseken, Smit, and Gaster (111) and Smit (486), however, obtained methyl 9,10,12,13-diepoxystearate by the epoxidation of methyl linoleate with peracetic acid in acetic acid solution, but yields were not reported. When this work was repeated in our laboratory (503), we found that the yield of product is extremely low, the major proportion of the methyl linoleate being converted to a polymer of unknown constitution. Subsequent investigators have reported that oxirane compounds can be obtained from a few unsaturated compounds by oxidation with peracetic acid in acetic acid solution, but yields have either not been reported or are low (30 per cent or less). Compounds epoxidized in this manner were 3,6-diacetoxy-5-methylnorcholestane (405), dihydrocaryophyllene (386), elaidic acid and methyl elaidate (297), ergosterol maleic-anhydride adduct (261), 5-methylnorcholestane-3,6-dione (405), β-amyrin acetate (492), and trans-7-octadecenoic acid (410).

In an important investigation, however, Arbuzow and Michailow (22) treated

TABLE 1

*Unsaturated substances converted to oxirane α-epoxy compounds by oxidation
with perbenzoic acid*

SUBSTANCE	REFERENCES
3(β)-Acetoxy-20-oxo-5-allo-Δ¹⁶-pregnene	(414)
Acetyllinaloöl	(431)
20-Allopregnene-3(β),17(β)-diol 3-monoacetate	(476b)
20-Allopregnene-3(β),17(β)-diol diacetate	(476b)
Allyl alcohol	(425, 430)
d-α-Amyrilene	(473)
β-Amyrilene	(473, 474)
β-Amyrin	(473, 474)
5-Androstene-3,17-dione	(465)
9-Androstene-3,17-dione	(412)
9-Androstene-3(β)-ol-17-one acetate	(453)
β-Anhydrodigoxigenin diacetate	(416)
β-Anhydrodihydrodigoxigenin diacetate	(416)
Anhydro-[4-(enol)acetobutyl alcohol]	(49, 51)
1-Anisyl-2,2-diphenylethylene	(311, 556)
1-Anisyl-1-(m-methoxyphenyl)ethylene	(321)
1-Anisyl-1 (o-methoxyphenyl)ethylene	(321)
Apocholenic acid	(566)
Apocholic acid	(126, 162, 567)
Benzaldehyde phenylhydrazone	(54)
1-Benzyl-1-cyclohexene	(369)
1-Benzyl-2,2-diphenylethylene	(311)
Benzylethylene	(323, 325)
Benzylideneacetone	(431)
1-(2-Biphenylyl)-1-phenyl-2,2-diethylethylene	(133)
Brassidic acid	(196)
p-Bromobenzylethylene	(439)
4-(p-Bromophenyl)-1-butene	(439)
Butadiene	(438)
1-Butyl-1-cyclohexene	(369)
1-Butyl-2,2-diphenylethylene	(311)
1-Isobutyl-2,2-diphenylethylene	(311)
C₁₈H₂₄ (two C=C)	(313)
Camphene	(208)
Caprylene	(425, 428)
d-3-Carene	(22)
Carotene	(207)
Caryophyllene	(476, 536)
1-Chloro-1-cyclohexene	(369, 373)
1-Chloro-2-cyclohexene	(371, 373)
1-Chloro-1-cyclopentene	(373)
1-Chloro-2-cyclopentene	(373)
1-Chloro-1-heptene	(426)
2-Chloro-1-methyl-1-cyclohexene	(373)
3-Chloro-1-methyl-3-cyclohexene	(371, 373)
1-Chloromethyl-2-phenylethylene	(220)
2-Chloro-1-methylenecyclohexane	(374)
2-Chloro-2-octene	(426)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
4-Cholestene	(247, 413)
5-Cholestene	(413, 467)
Δ⁵-Cholesten-3-one	(465)
γ-Cholestenyl acetate	(159a)
Cholesterol	(413, 465, 559)
Cholesteryl acetate	(465)
Cholesteryl benzoate	(261, 493)
Cholesteryl chloride	(247)
Cinnamyl acetate	(273)
Cinnamyl alcohol	(273)
Citral	(425, 431)
Citronellal	(425, 430)
Citronellol	(308a)
Copaene	(139a)
Crotonic acid	(136)
Crotyl alcohol	(273)
Cycloheptene	(94)
1,3-Cyclohexadiene	(43)
Cyclohexene	(85, 308)
Cyclopentene	(85)
1-Decene	(464)
Decene	(425)
Dehydroandrosterone	(538, 539)
3-*trans*-Dehydroandrosterone	(351)
trans-Dehydroandrosterone acetate	(469)
Dehydroergosteryl acetate–maleic anhydride adduct	(261)
Dehydroisoandrosterone	(201)
Dehydroisoandrosterone acetate	(200)
3,6-Diacetoxy-5-methylnorcholestane	(405)
3(β),21-Diacetoxy-20-oxo-5-allo-Δ¹⁴,¹⁶-pregnadiene	(415)
3,4-Diacetoxystyrene	(281a)
Diallyl	(84)
1,1-Dibenzyl-2-anisylethylene	(521)
1,1-Dicyclohexylethylene	(547)
Dicyclopentadiene	(38, 564)
1,1-Diethoxy-2-butene	(220)
1,1-Diethyl-2-anisylethylene	(521)
1,1-Diethyl-2-phenylethylene	(326)
Dihydro-β-amyrilene	(474)
Dihydrocaryophyllene	(476)
Dihydrocyclopentadiene	(564)
1,2-Dihydronaphthalene	(512)
2,3-Dihydronaphthalene	(93)
1,4-Dihydronaphthalene	(93, 512)
5,6-Dihydro-1,2-pyran	(401)
3,7-Dihydroxycholenic acid	(565)
4,5-Dihydroxy-2,6-octadiene	(273)
2,3-Dihydroxy-1-propene (acetone compound)	(218)
Diisobutylene	(425, 429)
1,1-Dimethyl-2-anisylethylene	(515, 521, 522)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
2,3-Dimethyl-2-butene	(429)
Dimethylcyclohexene	(429)
1,2-Dimethylcyclohexene	(381)
1,3-Dimethyl-1-cyclohexene	(369)
2,4-Dimethyl-1-cyclohexene	(369)
1,1-Dimethyl-2,2-diphenylethylene	(441)
1,2-Dimethyl-1,2-diphenylethylene	(441)
1,1-Dimethyl-2-(*m*-methoxyphenyl)ethylene	(320)
1,1-Dimethyl-2-(*o*-methoxyphenyl)ethylene	(320)
1,1-Dimethyl-2-methyl-2-phenylethylene	(334)
1,1-Dimethyl-2-phenylethylene	(326, 515, 522)
1,1-Dimethyl-2-piperonylethylene	(516, 520)
1,1-Dimethyl-2-tolylethylene	(516, 519)
2,4-Dimethyl-4-vinyl-1-cyclohexene	(313)
1,1-Dipropyl-2-anisylethylene	(521)
1,1-Di-*p*-tolylethylene	(442)
1-Dodecene	(40, 464)
Elaidic acid	(24, 38, 88, 502)
3,9-Epoxy-Δ^{11}-cholenic acid	(340)
Erucic acid	(38, 196)
1-Ethoxy-2-cyclohexene	(370)
Ethyl acetoacetate	(101)
1-Ethyl-2-anisylethylene	(216)
1-Ethyl-1-benzyl-2-phenylethylene	(326)
1-Ethyl-2-(*p*-bromophenyl)ethylene	(439)
Ethyl cinnamyl ether	(190)
1-Ethyl-2,2-dianisylethylene	(555)
1-Ethyl-2,2-diphenylethylene	(311, 319, 555)
Ethyl elaidate	(88)
1-Ethyl-1-ethoxy-2,2-dipropylethylene	(36)
Ethyl hendecenoate (undecylenate)	(327)
Ethyl 9,12,15-octadecatrienoate (linolenate)	(39)
Ethyl oleate	(37, 38, 39, 88)
1-Ethyl-2-phenyl-2-anisylethylene	(555)
1-Ethyl-2-phenylethylene	(316)
1-Ethyl-2-propyl-2-anisylethylene	(554)
Ethyl vinyl ether	(50)
11-Etiocholen-3(α)-ol-17-one acetate	(311a)
Δ^9-Etiocholen-3(α)-ol-17-one	(194)
Furfural diacetate	(484)
Furfural phenylhydrazone	(54)
Geraniol	(308a, 425, 428, 431)
Glucal	(52, 53)
1-Hendecene	(464)
Hendecenoic (undecylenic) acid	(237)
1-Heptene	(322)
1-Isoheptene	(322)
3-Heptene	(209)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
3(α)-Hydroxy-$\Delta^{9,11}$-cholenic acid	(340)
3(α)-Hydroxy-Δ^{11}-cholenic acid	(341)
11-Hydroxy-11,11-diphenyl-1-hendecene	(327)
11-Hydroxy-1-tetradecene	(327)
11-Hydroxy-1-tridecene	(327)
Indene	(38, 85, 93, 369)
α-Ionone	(387)
β-Ionone	(387)
Isodihydroxycholenic acid	(568)
Isoprene	(438, 456)
Isosafrole	(516)
Isostilbene	(295)
11-Keto-11-phenyl-1-hendecene	(327)
11-Keto-1-tetradecene	(327)
11-Keto-1-tridecene	(327)
Lanostenone	(44)
Lanosteryl acetate	(44, 197)
Limonene	(23, 346, 425, 428)
Linaloöl	(385, 425, 431)
Linolenic acid	(37, 39)
3-p-Menthene	(511)
1-Menthen-6-ol	(433)
Methyl $\Delta^{14,16}$-3(β)-acetoxyalloetiocholadienate	(472a)
Methyl 3(α)-acetoxy-$\Delta^{9,11}$-cholenate	(261, 484a)
Methyl 3(α)-acetoxy-Δ^{11}-cholenate	(420)
Methyl 3(β)-acetoxy-Δ^{11}-cholenate	(420)
Methyl 3(α)-acetoxy-12(α)-hydroxy-Δ^{7}-cholenate	(56b)
1-Methyl-2-anisylethylene	(316)
1-Methyl-1-benzyl-2-phenylethylene	(326)
Methyl brassidate	(196)
1-Methyl-2-(p-bromophenyl)ethylene	(439)
Methyl Δ^{9}-cholenate	(454)
Methyl Δ^{11}-cholenate	(4)
Methyl cinnamyl ether	(190, 273)
3-Methylcyclohexanone (enol acetate)	(372)
1-Methyl-1-cyclohexene	(85, 308, 335, 383)
4-Methyl-1-cyclohexene	(369, 379)
5-Methyl-1-cyclohexene	(308)
6-Methyl-1-cyclohexene	(308)
1-Methyl-1-cyclopentene	(85, 335)
d-3-Methyl-1-cyclopentene	(369)
4-Methyl-1-cyclopentene	(369)
Methyl diacetylapocholate	(568)
Methyl 3(α),12(β)-diacetylapocholate	(417)
Methyl Δ^{14}-3(α),12(β)-diacetoxycholenate	(417)
Methyl $\Delta^{7,14}$-3(α),12(β)-diacetoxycholadienate	(417)
1-Methyl-2,2-dianisylethylene	(555)
Methyl d-dihydropimarate	(466)
Methyl 3,7-dihydroxycholenate	(126)

TABLE 1—*Continued*

SUBSTANCE	REFERENCES
1-Methyl-2,2-diphenylethylene	(311, 319, 555)
1-Methyl-1,2-diphenylethylene	(517)
Methyl elaidate	(38)
Methylenecyclohexane	(523)
2-Methylenedecahydronaphthalene	(369)
Methyl erucate	(196)
1-Methyl-1-ethyl-2-anisylethylene	(554)
1-Methyl-2-ethyl-2-anisylethylene	(554)
4-Methyl-2-ethylcyclohexene	(369)
3-Methyl-1-ethylidenecyclohexane	(368, 369)
1-Methyl-1-ethyl-2-phenylethylene	(326)
Methyl hendecenoate (undecylenate)	(327)
Methyl heptenone	(430)
Methyl 2,4-hexadienoate (sorbate)	(248, 250)
Methyl 3(α)-hydroxy-Δ^{11}-cholenate	(420)
Methyl 3(β)-hydroxy-Δ^{11}-cholenate	(420)
Methyl 3(α)-hydroxy-12-methoxy-$\Delta^{9,11}$-cholenate	(478)
Methyl 3-keto-Δ^{11}-cholenate	(157)
Methyl 3-keto-$\Delta^{4,11}$-choladienate	(157)
Methyl 12-methoxy-$\Delta^{9,11}$-cholenate	(478)
3-Methyl-1-methylenecyclohexane	(369)
3-Methyl-1-methylenecyclopentane	(369)
Methyl 9,11-octadecadienoate	(341, 486)
Methyl 9,12-octadecadienoate (linoleate)	(111, 231, 411, 486)
Methyl oleate	(508)
Methyl petroselaidate	(498)
Methyl petroselinate	(498)
1-Methyl-1-phenylethylene	(46a, 180)
1-Methyl-2-phenylethylene	(46a, 316, 519)
Methyl d-pimarate	(466)
4-Methyl-2-propyl-1-cyclohexene	(369)
1-Methyl-1-propyl-2-phenylethylene	(326)
Methyl ricinelaidate	(111, 486)
Methyl ricinoleate	(486)
Methyl styryl carbinol	(375)
1-Nonene	(464)
9-Octadecene	(88)
Octenes	(407)
Oleic acid	(37, 38, 39, 88, 408, 447, 502, 508)
Oleyl alcohol	(504, 508)
1-Phenyl-2-anisylethylene	(515, 518)
1-Phenyl-2-benzylethylene	(316)
cis-Phenylbutadiene	(376)
4-Phenyl-1-butene	(323, 325)
1-Phenyl-1-cyclohexene	(85, 324, 335, 382)
1-Phenyl-1-cyclopentene	(85, 335)
1-Phenyl-2,2-dibenzylethylene	(515, 518)
6-Phenyl-1-hexene	(323, 325)
1-Phenyl-1-(m-methoxyphenyl)ethylene	(321)

TABLE 1—*Concluded*

SUBSTANCE	REFERENCES
1-Phenyl-1-(o-methoxyphenyl)ethylene	(321)
1-Phenyl-4-methylcyclohexene	(324)
5-Phenyl-1-pentene	(323, 325)
1-Phenyl-2-piperonylethylene	(516, 520)
1-Phenyl-2-(p-tolyl)ethylene	(516, 519, 556)
Pinene	(208, 384, 425, 428, 432)
5-Pregnen-20-one-3(β),21-diol 21-monoacetate	(200)
2-Propenyldioxolane	(220)
1-n-Propyl-2-anisylethylene	(316)
1-n-Propyl-1-benzyl-2-phenylethylene	(326)
1-Isopropyl-1-benzyl-2-phenylethylene	(326)
1-n-Propyl-1-cyclohexene	(369)
1-Isopropyl-1-cyclohexene	(369)
1-n-Propyl-1-cyclopentene	(369)
1-Isopropyl-1-cyclopentene	(369)
1-n-Propyl-2,2-diphenylethylene	(311)
1-Isopropyl-2,2-diphenylethylene	(311)
1-n-Propyl-2-phenylethylene	(316)
1-Isopropyl-2-phenylethylene	(316)
Pulegone	(427)
Rubber	(435, 436)
Squalene	(447)
Stilbene	(95, 295, 447, 515)
Styrene	(46a, 93, 258, 259 281a, 447)
1,2,3,4-Tetrahydronaphthalene	(308)
Tetraphenylethylene	(318)
Thiopyrine	(306)
1-Tridecene	(464)
1,2,5-Trimethyl-5-isopropenyl-1-cyclohexene	(313)
Triphenylethylene	(311, 556)

d-Δ³-carene with a solution of peracetic acid in acetic acid solution and also with an ether solution of peracetic acid. With the first oxidizing solution they obtained hydroxyacetates, whereas with the second they obtained good yields of oxirane compound. Similarly, α-pinene is converted to the oxirane compound in 89 per cent yield by means of peracetic acid in ether solution. With peracetic acid in chloroform solution α-pinene, however, is converted to the oxirane compound in only fair yield, the major proportion of the product being converted to the hydroxyacetate. In a subsequent report (23), these investigators extended their work to other olefins, and demonstrated that limonene, cyclohexene, anethole, and isoeugenol can be converted to oxirane compounds in good yield by employing an ether solution of peracetic acid. They concluded, therefore, that the behavior of peracetic acid toward olefins is the same as that of perbenzoic acid—namely, it converts the double bond to the oxirane group—but when an acetic acid solution of peracetic acid is employed, the oxirane compound is converted to the hydroxyacetate by further reaction with the acetic acid.

Peracetic acid in an inert solvent has also been applied by Böeseken and Schneider (104) to the epoxidation of cyclohexene, stilbene, and isostilbene, by Pigulevskiĭ (407) to the epoxidation of octenes, and by Tanaka (511) to the epoxidation of stilbene and 3-p-menthene.

TABLE 2

Unsaturated substances converted to oxirane (α-epoxy) compounds by oxidation with monoperphthalic acid

SUBSTANCE	REFERENCES
3(β)-Acetoxy-20-oxo-5-allo-Δ^{14,16}-pregnadiene	(414)
20-Allopregnene-3(β),17(β)-diol	(294a, 484a)
1-(2-Biphenylyl)-1-phenyl-2,2-dimethylethylene	(133)
Capsanthin diacetate	(287)
α-Carotene	(285)
β-Carotene	(284)
Cholesterol	(167)
Cholesteryl acetate	(167, 413)
Cholesteryl benzoate	(41, 167)
Cryptoxanthin diacetate	(288)
trans-Dehydroandrosterone acetate	(469, 471)
trans-Dehydroandrosterone benzoate	(469)
3(β),21-Diacetoxy-20-oxo-5-allo-Δ^{14,16}-pregnadiene	(415)
α-Elemolic acid	(472b)
α-Ionone	(292)
β-Ionone	(292)
Linaloöl	(385)
2-Lupene	(274a)
Methyl Δ^{14}-3(β)-acetoxyalloetiocholenate	(416)
Methyl Δ^{14,16}-3(β)-acetoxyetiocholadienate	(472)
Methyl Δ^{14}-3(β)-acetoxy-17-isoalloetiocholenate	(416)
Methyl α-elemolate	(472b)
Methyl α-ionone	(387)
Methyl d-pimarate	(475)
1-Phenyl-2-cyclohexylethylene	(514)
Δ^{14,17}-Pregnadien-3-one	(468)
Rubixanthin	(290)
Vitamin A	(286, 289)
Xanthophyll diacetate	(283)
Zeaxanthin diacetate	(283)

The apparent necessity for employing peracetic acid in an inert solvent to obtain good yields of oxirane compounds from olefins was a serious drawback to the general applicability of peracetic acid for epoxidation, since peracetic acid can be prepared and used most conveniently in acetic acid solution, whereas its isolation free (or substantially free) of acetic acid is accomplished only with great difficulty. In connection with a kinetic study of the reaction of peracetic acid (approximately 1 molar) in acetic acid solution with various long-chain compounds having isolated, non-terminal double bonds, Findley, Swern, and Scanlan (217) observed that if the temperature is maintained between 20° and 25°C.

consumption of peracetic acid is substantially complete in 2–4 hr. when only 1.1–1.2 moles of peracetic acid per mole of double bond is employed, 85–95 per cent of the theoretical quantity of peracetic acid being consumed. The products isolated consisted of oxirane compounds containing only small amounts of hydroxyacetate and unreacted olefin. The reaction was shown to be a general one and afforded a simple and convenient method for the preparation of large quantities of oxirane compounds, and isolation of peracid and employment of inert solvents were unnecessary. This reaction was successfully applied (217) to the epoxidation of oleic acid, methyl oleate, elaidic acid, methyl hendecenoate (undecylenate), methyl ricinoleate. oleyl alcohol, triolein, lard oil, neatsfoot oil, olive oil, peanut oil, cottonseed oil, corn oil, soybean oil, tobaccoseed oil, menhaden oil, linseed oil, perilla oil, castor oil, and rapeseed oil. In a later investigation, Swern, Billen, and Scanlan (506) converted 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene to the corresponding oxirane compounds in fair yields by epoxidation with peracetic acid in acetic acid solution. The terminally unsaturated compounds require about 24 hr. reaction time, as compared with 2–4 hr. for olefins with non-terminal, isolated double bonds.

Comparison of the reaction conditions employed by Swern and coworkers (217, 506) with those employed by earlier investigators who studied the oxidizing action of peracetic acid in acetic acid solution on olefins reveals the reason for the failure of the earlier workers to obtain high yields of oxirane compounds. Swern and coworkers employed relatively short reaction periods and low temperatures, whereas the earlier investigators usually employed either long reaction periods at room temperature or short reaction periods at elevated temperatures, or the solution contained sulfuric acid (employed as the catalyst in the preparation of peracetic acid). Thus, Findley, Swern, and Scanlan (217) reported that certain long-chain oxirane compounds dissolved in a large excess of glacial acetic acid are converted to hydroxyacetates at the rate of about 1 per cent per hour at 25°C., but at 65°C. the conversion to hydroxyacetates is complete in only 4 hr., and at 100°C. it is complete in 1 hr. Furthermore, when peracetic acid solutions in glacial acetic acid containing 1 per cent of concentrated sulfuric acid are employed in epoxidation reactions, no oxirane compounds can be isolated and quantitative yields of hydroxyacetates are obtained, even when mild reaction conditions are employed (217, 506). The sulfuric acid catalyzes the ring-opening reaction of acetic acid with the oxirane group. Under the proper reaction conditions, however, peracetic acid in acetic acid solution can be employed as a general reagent for the epoxidation of the isolated double bond.

d-Pinene epoxide and cholesterol epoxide have also been prepared by the reaction of the corresponding unsaturated compounds with percamphoric acid (357).

2. Preparation of α-glycols

The utilization of peracetic acid for the preparation of α-glycols from unsaturated compounds far exceeds that of all other organic peracids combined. This peracid is usually employed in one of two ways. It is either preformed by the reaction of acetic acid or acetic anhydride with hydrogen peroxide, or the

unsaturated compound is mixed with hydrogen peroxide and acetic acid (with or without a sulfuric acid catalyst), and the peracetic acid is consumed as it is formed. In these reactions, the olefin is first converted to the oxirane compound, which can be isolated if no strong acid catalyst has been employed, if the reaction conditions are mild, and if the reaction is of sufficiently short duration (see earlier discussion). If the reaction mixture is heated at 65°C. for 4 hr. or 100°C. for 1 hr., the oxirane compound (in solution) is quantitatively converted to the hydroxy-acetate, which in turn can be readily hydrolyzed to the α-glycol in quantitative yield. If the peracetic acid solution contains sulfuric acid, the oxirane compound is rapidly and quantitatively converted to the hydroxyacetate in a few hours even at 40°C. In many cases in which the oxirane compound has been isolated, it has also been converted to the α-glycol in excellent yield. Most investigators have effected this hydrolysis by means of concentrated alkali, although other techniques are preferable (502).

Although peracetic acid can be prepared by efficient processes, and only a small proportion of active oxygen is lost or unavailable for oxidative purposes, the separate preparation of the peracid is a time-consuming step in the hydroxyla-tion reaction. In an attempt to obviate the need for isolating peracetic acid, some workers have employed a solution of hydrogen peroxide in acetic acid to hy-droxylate olefins. As employed by earlier workers, the reaction mixture or solu-tion of 25–30 per cent hydrogen peroxide, acetic acid, and olefinic compound is allowed to stand at room temperature for long periods (262, 264), the reaction mixture is heated to accelerate peracid formation (262, 264), or the hydrogen peroxide and acetic acid are preheated to form peracetic acid, followed by addi-tion of the compound to be hydroxylated without attempting to maintain the temperature below 40°C. (479, 480). By these procedures much active oxygen is lost, and although excellent yields of α-glycol can be obtained, a large excess of hydrogen peroxide must be employed. Recently, Swern and coworkers (505) demonstrated that by treating the olefin with 25–30 per cent hydrogen peroxide and acetic acid containing catalytic quantities of concentrated sulfuric acid, excellent yields of α-glycols can be obtained with the use of approximately stoi-chiometric quantities of hydrogen peroxide. Since the mineral acid catalyzes peracetic acid formation and since the peracid is rapidly consumed at 40°C., the reaction is complete in a few hours and little active oxygen is lost. This hydroxylation method is one of the most efficient for converting long-chain olefinic compounds to α-glycols. Recently, Greenspan (232) was able to achieve more complete hydroxylation with 90 per cent hydrogen peroxide instead of 25–30 per cent.

Numerous unsaturated substances have been hydroxylated by oxidation with peracetic acid, either preformed or by formation and utilization *in situ*. These substances are listed alphabetically in table 3. It is obvious that oxirane com-pounds prepared by the peracetic acid oxidation of olefins (already discussed) can be converted to α-glycols, and some earlier workers concerned primarily with the preparation of oxirane compounds have made the α-glycols from them. These unsaturated compounds are not listed in this table, since they have already been

TABLE 3

Unsaturated substances converted to α-glycols by oxidation with peracetic acid

SUBSTANCE	REFERENCES
Allostilbene	(95)
Allylacetic acid	(103)
Allylbenzene	(96)
Allylmalonic acids	(103)
Anethole	(96)
Benzyl 2-propenyl sulfone	(544)
Brassidic acid	(196)
Butadiene sulfone	(544)
2-Butene	(90)
d-Δ¹-Carene	(412)
d-Δ⁸-Carene	(22)
Castor oil	(294, 480, 481, 482)
Cholesterol	(412a)
Cholesteryl acetate	(406)
Cocoa butter	(264)
Cyclohexene	(23, 96, 483)
3-trans-Dehydroandrosterone	(351)
3-trans-Dehydroandrosterone tetraacetylglucoside	(351)
Dehydroisoandrosterone acetate	(199)
Diisobutylene	(160, 260, 269)
Dimethylbutadiene sulfone	(544)
Isododecene	(269)
11,12-Eicosenoic acid	(267)
Elaidic acid	(24, 196, 262, 297, 394, 486, 502, 505)
Eleostearic acid	(99)
Eleostearic acid dibromide	(99)
Eleostearic acid tetrabromide	(99)
Erucic acid	(196, 463)
Ethyl elaidate	(486)
Ethyl eleostearate	(99)
Ethyl oleate	(479, 481, 482, 486)
Eugenol	(96)
Hendecenoic (undecylenic) acid	(103, 463)
Hendecenoic acid dimers	(463)
1-Heptene	(86)
3-Heptene	(86)
1-Hexadecene	(120, 235)
Indene	(96)
Isoprene	(86)
β-Isoprene sulfone	(544)
Isosafrole	(96)
Limonene	(509)
Linoleic acid	(231, 489)
3-Menthene	(483)
Methyl brassidate	(196)
1-Methyl-1-cyclohexene	(483)
3-Methyl-1,2-butadiene (dimethylallene)	(86)

TABLE 3—*Concluded*

SUBSTANCE	REFERENCES
Methyl elaidate	(262, 265)
Methyl erucate	(196)
2-Methyl-1-heptene	(86)
Methyl linoleate	(231)
Methyl oleate	(262, 265, 297)
Methyl palmitoleate	(262)
Methyl petroselinate	(263)
Isononene	(269)
Norbornylene	(70a)
9,11,13-Octadecatrienol (eleostearyl alcohol)	(491)
Oleic acid	(46, 196, 232, 262, 297, 394, 479, 481, 482, 486, 502, 505)
Oleyl alcohol	(479, 481, 482, 491)
Phenylbenzylethylene	(96)
Pregnenonol acetate	(199)
Ricinelaidic acid	(294)
Ricinoleic acid	(294)
Ricinoleyl alcohol	(491)
Safrole	(96)
Sorbic acid	(103)
Soybean oil	(270, 271, 272, 395)
Stilbene	(95)
Tallow	(264)

mentioned. Some of the unsaturated substances listed in table 3 have been converted to hydroxyacetates rather than to α-glycols, but the conversion of the acetate to the glycol is effected so readily that it was deemed desirable to include these substances.

Since the reaction of hydrogen peroxide with organic acids is an equilibrium reaction, the hydrogen peroxide will be completely consumed if the peracid reacts as it is formed. If reaction conditions favor rapid formation of the peracid without causing decomposition, stoichiometric utilization of the active oxygen should be feasible, since peracids react rapidly with many classes of oxidizable substances. With most aliphatic acids, however, formation of peracid is a relatively slow reaction at moderate temperatures. Thus, D'Ans and Frey (184) have shown that the reaction of approximately equimolar quantities of substantially anhydrous hydrogen peroxide and acetic, propionic, or butyric acid requires 12–16 hr. for attainment of equilibrium even when sulfuric acid is employed as catalyst. Unlike these aliphatic acids, however, formic acid reacts rapidly with hydrogen peroxide at moderate temperatures, yielding performic acid, and equilibrium is attained in less than 2 hr. with either 90–100 per cent hydrogen peroxide (184, 233) or even with 25–30 per cent hydrogen peroxide (507, 525). Swern and coworkers (505) have taken advantage of the unusual reactivity of formic acid and demonstrated that performic acid (507) or, preferably, 25–30 per cent hydrogen peroxide and formic acid (505), can be employed as an extremely efficient

hydroxylating reagent for the isolated double bond. These investigators obtained substantially quantitative conversion to the α-glycol in a short time, employing approximately stoichiometric quantities of hydrogen peroxide. The initial product of oxidation, however, is not the α-glycol but the oxirane compound, which is rapidly converted to hydroxyformates as a result of the high acidity of formic acid. The hydroxyformates are the products isolated and these are readily converted to the α-glycol by hydrolysis with dilute aqueous alkali or even by exposure to moist air or heating with water (502). This hydroxylation technique, which is probably the most efficient one known for long-chain unsaturated compounds with isolated double bonds, was applied by Swern and coworkers (505) to the oxidation of oleic acid, elaidic acid, oleyl alcohol, methyl ricinoleate and 10,11-hendecenoic (undecylenic) acid, and subsequently (506) to 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. Although solutions of performic acid can be separately prepared and then employed for hydroxylation purposes, its relative instability, as compared with peracetic acid and other aliphatic peracids (165, 189, 204, 233, 507, 525), causes appreciable quantities of active oxygen to be lost, and procedures in which previously prepared performic acid is employed are much less efficient, in general, than those in which performic acid is prepared and utilized *in situ.*

Recently, Greenspan (232) substituted 90 per cent hydrogen peroxide for the 25–30 per cent concentration and obtained slightly more complete reaction in the hydroxylation of oleic and 10,11-hendecenoic (undecylenic) acids. Also, English and Gregory (204) showed that concentrated performic acid can be used in the hydroxylation of α,β-unsaturated acids, giving the dihydroxy acids in fair yields, generally, within a relatively short time. Earlier workers, who had employed dilute peracids, had either been unable to hydroxylate such compounds or extremely long reaction times were required, with concomitant loss of active oxygen. α,β-Unsaturated compounds hydroxylated by English and Gregory (204) were 2-nonenoic, 2-hendecenoic, and cinnamic acids, and dimethyl traumatate and methyl 2-nonenoate. They also hydroxylated cyclohexene, obtaining good yields of *trans*-1,2-cyclohexanediol.

The early work of Isii (271) on the hydroxylation of soybean oil with performic acid, as well as with other organic peracids, is worthy of mention. No definite products were obtained, although he showed that the acetyl number of the treated soybean oil was higher than that of the original.

Recently, Weitkamp and coworkers (557) treated some monounsaturated acids obtained from human hair fat with hydrogen peroxide and formic acid and obtained the corresponding dihydroxy acids.

Although perbenzoic, monoperphthalic, and percamphoric acids are ordinarily not considered to be hydroxylating reagents, since the products usually obtained in the oxidation of olefins with these oxidants are the oxirane compounds, these peracids can be employed in the preparation of glycols, since the oxirane compound can be converted to the α-glycol in quantitative yield. In some cases this series of reactions has been carried out. In general, there is no advantage whatsoever in employing the aromatic peracids to prepare α-glycols when two more

efficient peracids are available for this purpose—namely, performic and peracetic acids, either preformed or prepared and used *in situ*. Under some reaction conditions, however, perbenzoic acid has converted the double bond either to the α-glycol group or to a benzoate ester readily hydrolyzable to the α-glycol, and oxirane compounds are not isolated. In these cases, water has been present or reaction times have been exceptionally long. Unsaturated substances which have

TABLE 4

Unsaturated substances converted to α-glycols by oxidation with perbenzoic acid

SUBSTANCE	REFERENCES
Anhydroacetobutyl alcohol	(49)
Apocholic acid	(162, 567)
Cellobial	(53)
2,4-Cholestadiene	(56)
Crotonic acid	(135)
Dihydroergosteryl acetate	(574)
1,1-Diphenylethylene	(390)
Elaidic acid	(394)
Ergosterol	(574)
α-Ergostenyl acetate	(574)
Furan	(117)
Galactal	(315)
Glucal	(52, 510)
2-Hexenoic acid	(137)
Isocrotonic acid	(135)
Lactal	(48)
Linoleic acid	(409)
Methyl dihydroxycholenate	(162)
3-Methylglucal	(314)
Oleic acid	(394)
2-Pentenoic acid	(137)
cis-Phenylbutadiene	(376)
Rhamnal	(52, 53)
Ricinelaidic acid	(38)
Ricinoleic acid	(38)
1,2,3,4-Tetracetyl-1,2-glucosene	(494)
Triacetylgalactal	(315)
Triacetylglucal	(314, 510)

been converted to α-glycols or to hydroxybenzoates by oxidation with perbenzoic acid are listed in table 4.

3. Miscellaneous

The peracid oxidation of compounds containing aromatic double bonds has also been studied. Henderson and Boyd (251) treated numerous phenols with 30 per cent hydrogen peroxide in acetic acid solution and obtained quinones or dihydric and tetrahydric phenols. The initial stage of the reaction seems to involve oxidation at a double bond. Phenols studied were phenol, *o*-, *m*-, and

p-cresols, p-tert-butylphenol, 3,5-diethylphenol, carvacrol, and thymol. They also reported that benzene, toluene, and 1,3-diethylbenzene are not attacked but that naphthalene, anthracene, and phenanthrene are readily oxidized yielding phthalic acid, anthraquinone, and phenanthraquinone, respectively. Recently Greenspan (232), employing concentrated peracetic acid, obtained anthraquinone in good yield from anthracene. Charrier and Moggi (171) duplicated some of the work of Henderson and Boyd (251) and confirmed the fact that hydrogen peroxide in acetic acid solution converts naphthalene and anthracene to phthalic acid and anthraquinone, respectively, but they reported that benzene is slowly oxidized to carbon dioxide, water, and a resinous material, and that phenanthrene is converted to diphenic acid (phenanthraquinone is postulated as an intermediate). They also demonstrated that 2-N-phenyl-α,β-naphthotriazole yields o,o'-2-N-phenyltriazolephenyldicarboxylic acid. Although Böeseken and Slooff (110) confirmed the fact that phenanthrene yields diphenic acid on oxidation with peracetic acid, they reported that naphthalene is converted to o-carboxyallocinnamic acid and not to o-phthalic acid, that benzene is stable toward this oxidizing agent, and that anthracene, although it reacts, does not yield anthraquinone. In view of Greenspan's recent work with anthracene (232), this last observation of Böeseken and Slooff (110) cannot be accepted. Later, Böeseken and Engelberts (83, 96a) confirmed the fact that benzene is not attacked by peracetic acid, and showed that phenol is converted to cis,cis-muconic acid (o-quinone intermediate) in excellent yield and that some benzoquinone is also obtained. Catechol (83) is also converted to muconic acid, as well as to carbon dioxide and fumaric acid, and hydroquinone yields quinhydrone and fumaric acid. α-Naphthol (118) is converted in poor yields to o-carboxyallocinnamic acid, coumarin, α-naphthoquinone, and a resin reported to be a polymer of α-naphthoquinone oxide. β-Naphthol (63, 118), however, is converted to o-carboxyallocinnamic acid in good yield, some tetrahydroxynaphthalene and an acid ($C_{20}H_{12}O_4$) also being formed. Greenspan (232) has recently confirmed the fact that o-carboxyallocinnamic acid is formed in good yield when β-naphthol is oxidized with peracetic acid. In a similar manner, Bigiavi and Cerchiai (63) obtained o-carboxyallocinnamic acid from 1-benzeneazo-2-naphthol on oxidation with cold peracetic acid or with hydrogen peroxide and acetic acid, and obtained dihydroisocoumarincarboxylic acid when hot peracetic acid was employed. Grundmann and Trischmann (236) reported that o-coumaric acid is converted to cis,cis-muconic acid in small yield by peracetic acid and that 2,2'-dihydroxydiphenyl yields two products which are probably 2'-hydroxy-2-phenylquinone and α-(hydroxyphenyl)muconic lactone. 1,8-Dihydroxynaphthalene (112) is resinified by peracetic acid, but its monomethyl ether yields a mixture of 8-methoxy-α-naphthoquinone and a dehydration product of methoxy-3-carboxyallocinnamic acid. p-Cymene (222) is oxidized in poor yields to carvacrol, thymohydroquinone, and thymoquinone by hydrogen peroxide and acetic acid. When ferrous sulfate is added to the peracetic acid, p-isopropylbenzaldehyde is obtained. With an excess of peracid, the quinones which form in the reactions just described are cleaved to dibasic acids (Section III, E).

The peracid oxidation of unsaturated compounds in which the double bond is adjacent to a carbonyl group ($-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$) represents an unusual reaction. In the oxidation of such compounds, an oxygen atom is introduced between the carbonyl group and the ethylenic carbon atom ($-\overset{|}{C}=\overset{|}{C}-O-\overset{|}{C}=O$). Böeseken and coworkers (100, 102, 113), who are apparently the only investigators who studied this reaction, converted benzalacetone to β-phenylvinyl acetate (acetate of enolized phenylacetaldehyde), and obtained similar oxidation products from α-methyl-α-benzalacetone and from benzalmethyl ethyl ketone. The formation of the oxidation products is not a secondary reaction resulting from the isomerization of an oxirane compound,

$$-\overset{|}{\underset{\diagdown}{C}}---\overset{|}{\underset{\diagup}{C}}-\overset{|}{C}=O$$
$$O$$
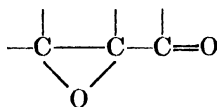
since such a compound, prepared from benzalacetone by oxidation with alkaline hydrogen peroxide (558), is unaffected by peracetic acid under the reaction conditions employed.

In two cases (benzaldehyde phenylhydrazone and furfural phenylhydrazone, table 1), the carbon–nitrogen double bond has been oxidized to the oxirane group by perbenzoic acid (54) but in other instances a different type of reaction has been reported. Bergmann, Ulpts, and Witte (54) oxidized benzanil with perbenzoic acid in ether solution and obtained nitrobenzene and benzaldehyde. Benzophenone phenylhydrazone, under similar conditions, yields benzophenone and benzoic acid. Botvinnik and coworkers (128, 129) studied the perbenzoic acid oxidation of carbon–nitrogen double bonds in imidazoles and similar substances, and reported marked degradation of the molecule.

A limited amount of work has been published on the oxidation of acetylenic compounds. When reaction occurs, these substances are cleaved to shorter chain-length fragments. Böeseken and Slooff (109) obtained good yields of pelargonic and azelaic acids from stearolic (9-octadecynoic) acid by oxidation with peracetic acid. 9-Hendecynoic acid is reported to yield suberic and formic acids, and 10-hendecynoic acid yields sebacic acid. They reported that acetylene and phenylacetylene do not react with peracetic acid, but Prileschajew (429) reported that phenylacetic acid is obtained from phenylacetylene by oxidation with perbenzoic acid.

Rubber is readily oxidized at −20°C. to +145°C. by organic peracids, including performic, peracetic, perpropionic, monochloroperacetic, dichloroperacetic, monobromoperacetic, and monobromoperpropionic acids (71, 337), or with hydrogen peroxide and acetic (337) or formic acid (71). No definite products were isolated, however.

Camphene (256) and β-pinene (253), on treatment with hydrogen peroxide and acetic acid at 60°C., yield many products consisting of acids, ketones, aldehydes, and alcohols. α-Pinene (257), however, when similarly treated, yields α-terpineol

as the main oxidation product. Bornylene (252) is converted to a mixture of acids, esters, and aldehydes, but no ketones are formed. Sabinene (254) and sabinol (255) yield two isomeric products which appear to be glycol anhydrides.

Diallyl has been reported to react normally with perbenzoic acid, but the expected dioxirane compound could not be isolated (84). On hydrolysis the oxidation products yield 2,5-di(hydroxymethyl)tetrahydrofuran.

In the peracid oxidation of furan and its derivatives, such as furfural, 2-methylfuran, and furfuryl alcohol, the major reaction is the formation of resins (117), but small quantities of formic, maleic, and aldehydomalic acids, and the anhydride of β-acetyllactic acid are also formed. Böeseken and coworkers (117) have concluded, therefore, that the initial oxidation products are labile oxirane compounds, which rapidly resinify to a great extent but also undergo cleavage and hydrolysis, yielding the identifiable products.

Komada (305) studied the oxidation of aminopyrine and antipyrine with perbenzoic acid and reported that the expected products are not obtained. Thiopyrine (306), however, yields a diepoxy derivative.

Elm (203) studied the perbenzoic acid oxidation of trilinolenin and reported that only six of the nine double bonds are attacked, and that keto rather than oxirane compounds are formed. No evidence was presented for this conclusion.

Methoxyethyl vinyl ether (273) is converted to the dimer of ethyl 2-methoxyglycoloside by perbenzoic acid in chloroform solution. 1-Phenyl-1-(2-biphenyl)-ethylene (132) adds two atoms of oxygen but the product is unidentified. Under certain conditions 1,1-diphenylethylene yields diphenylacetaldehyde (390). Methoxymethyldihydroneostrychnine (139, 166) adds two atoms of oxygen, yielding methoxymethylchanodihydrostrychnone.

Peracetic acid converts diisobutylene to an unsaturated alcohol, a glycol, and high-boiling products (160, 260). Vinyl halide polysulfones (339) are polymerized by perbenzoic or peracetic acid, and acetylursolic acid (274) is converted to a mixture of many products when treated at the boiling point with 30 per cent hydrogen peroxide and acetic acid.

Vinet and Meunier (548, 549) reported that, contrary to the observation of Karrer and Jucker (286, 289; table 2), vitamin A or its acetate on oxidation with monoperphthalic acid in ether solution yields a secondary alcohol and not an oxirane compound. Gridgeman and coworkers (234) oxidized β-carotene with perbenzoic acid in chloroform solution and reported the formation of a five-membered oxygen-containing ring.

Daniels and Levy (179a) prepared esters of valerolactone by treating esters of alkenylmalonic acids with peracids in the presence of strong mineral acid catalysts.

B. OXIDATION OF ORGANIC SULFUR COMPOUNDS

One of the most efficient and widely used reactions of organic peracids is the oxidation of organic sulfides and mercaptans to sulfoxides and sulfones. These reactions usually proceed at convenient temperatures, are rapid, and in most cases give very high or even quantitative yields of product. Perhaps the earliest

application of this reaction was reported by Hinsberg (266), who obtained good yields of the corresponding sulfoxides by the oxidation of dibenzyl sulfide, di-*p*-acetaminophenyl sulfide, diphenyl disulfide, and dibenzyl disulfide with hydrogen peroxide in acetic acid solution. With larger quantities of hydrogen peroxide, sulfones are obtained. Furthermore, the sulfoxides can be quantitatively converted to the sulfones by the same oxidant mixture. It is not essential to employ an organic acid as the solvent and oxygen-carrier (peracid intermediate) for these reactions, and inert solvents may be used (226, 457, 537), but the reactions are more satisfactory when an organic peracid (preferably prepared and utilized *in situ*) is the oxidant (228). Table 5 gives an alphabetical list of organic sulfur compounds converted to sulfoxides and/or sulfones by organic peracids.

Alkyl thiolsulfinates have been prepared (485) by the oxidation of aliphatic disulfides, such as dimethyl, diethyl, dipropyl, dibutyl, diamyl, and diallyl disulfides, with organic peracids. Perbenzoic acid is generally employed, but peracetic, perfuroic, perphthalic, and percamphoric acids can also be used. Perlauric acid, however, is not so satisfactory as the others.

Pomerantz and Connor (418) converted a series of α-alkylthioamides to the corresponding α-alkylsulfonamides in good yield by oxidation with a mixture of hydrogen peroxide, acetic acid, and acetic anhydride.

Surprisingly, 1,2-bis(2-diethylaminoethylmercapto)ethane hydrochloride, 1,2-bis(2-dibutylaminoethylmercapto)ethane hydrochloride, and 1,2-bis[2-(1-piperidyl)ethylmercapto]ethane hydrochloride are converted to the sulfone or sulfonic acid, with the loss of two methylene groups, when hydrogen peroxide and acetic acid at the boiling point are employed as the oxidizing agent (424).

C. OXIDATION OF ORGANIC NITROGEN COMPOUNDS

The oxidation of organic nitrogen compounds with organic peracids falls into three main classes: (*1*) oxidation of amines to nitroso, azo, azoxy, and nitro compounds, (*2*) oxidation of azo compounds to azoxy compounds, and (*3*) oxidation of amines to amine oxides.

1. Oxidation of amines to nitroso, azo, azoxy, and nitro compounds

Baeyer and Villiger (31, 33) observed that on oxidation with perbenzoic or monoperphthalic acid aniline is converted to nitrosobenzene, but yields were not reported. Prileschajew (425), however, reported that aniline yields azobenzene when treated with an equimolar quantity of perbenzoic acid and that nitrosobenzene and a little nitrobenzene are obtained when double the quantity of perbenzoic acid is employed. *o*-Toluidine yields *o*-nitrotoluene when similarly treated. Again, yields were not reported. Prileschajew also studied the oxidation of azoxybenzene and methylaniline, but did not report the products obtained.

D'Ans and Kneip (189) have stated that primary amines are converted to nitroso compounds on oxidation with peracids in the cold, but with concentrated peracids and without cooling the reaction mixture nitro compounds are obtained. By varying the quantity of peracid and the reaction conditions, azo and azoxy compounds can also be prepared. D'Ans and Kneip obtained fair yields of both

TABLE 5

Organic sulfur compounds converted to sulfoxides and/or sulfones by oxidation with organic peracids

SULFUR COMPOUND	REFERENCES
2-Acetylamino-4-methyl-4'-nitro-5-thiazolylphenyl sulfide	(35)
2-Acetylamino-4'-nitro-5-thiazolylphenyl sulfide	(35)
2-Acetylamino-4'-nitro-5-thiodiazolylphenyl sulfide	(35)
2-Acetylmethylamino-4-methyl-4'-nitro-5-thiazolylphenyl sulfide	(35)
ω-Alkylmercapto fatty acids	(443)
4-Aminodiphenyl sulfide	(229)
Benzyl carboxymethyl sulfide	(393)
8-Benzylthiocaffeine	(331b)
1,2-Bis(2-benzoxyethylmercapto)ethane	(423)
1,2-Bis(2-chloroethylmercapto)ethane	(423)
Bis(ethylthio)methane	(121, 477)
1,2-Bis(2-hydroxyethylmercapto)ethane	(423)
Bis(2-nitro-1-naphthyl)sulfide	(223a)
Bis(4-nitro-1-naphthyl)sulfide	(223a)
4-Bromo-4'-nitrodiphenyl sulfide	(5)
2-Bromo-8-nitrothiaxanthene	(4a)
n-Butyl 2-chloroethyl sulfide	(155a)
Isobutyl 2-chloroethyl sulfide	(155a)
Butyl 2-nitropropyl sulfide	(245a)
8-n-Butylthiocaffeine	(331b)
n-Butyl p-tolyl sulfide	(228)
Carboxymethyl 2-nitroethyl sulfide	(245a)
Casein	(524)
2'-Chloro-4-aminodiphenyl sulfide	(229)
3'-Chloro-4-aminodiphenyl sulfide	(229)
4'-Chloro-4-aminodiphenyl sulfide	(229)
p-Chlorobenzyl sulfidoacetic acid	(393)
4'-Chloro-2,4-diaminodiphenyl sulfide	(229)
3'-Chloro-2,4-dinitrodiphenyl sulfide	(229)
4'-Chloro-2,4-dinitrodiphenyl sulfide	(229)
2-(2-Chloroethylmercapto)ethyl ether	(422)
2-Chloroethyl p-tolyl sulfide	(228)
2-Chloro-2'-methylthiodiethyl sulfide	(154)
2'-Chloro-4 nitrodiphenyl sulfide	(229)
3'-Chloro-4-nitrodiphenyl sulfide	(229)
4'-Chloro-4-nitrodiphenyl sulfide	(229)
1-Chlorovinyl 2-chloroethyl sulfide	(331)
2-Chlorovinyl 2-chloroethyl sulfide	(331)
2-Crotonyl-4'-nitro-5-thiazolylphenyl sulfide	(35)
Cystine	(477a, 526, 527, 528, 529, 530)
2,8-Diacetamidothioxanthone	(6)
Di(p-acetylaminophenyl) sulfide	(266)
Diallyl sulfide	(330)
2,8-Diaminodibenzothiophene (tetraacetyl derivative)	(389)
Dibenzyl disulfide	(266)
Dibenzyl sulfide	(21, 122, 266, 328, 329, 457)

TABLE 5—*Continued*

SULFUR COMPOUND	REFERENCES
2,8-Dibromodibenzothiophene	(389)
2,2'-Dibromodiethyl sulfide	(330)
Di(p-bromophenyl) sulfide	(87, 457)
Di(2,4-dichlorobenzyl) sulfide	(393)
1,1'-Dichlorodiethyl sulfide	(330)
2,2'-Dichlorodiethyl sulfide	(328, 329)
1,1'-Dichlorodimethyl sulfide	(328, 330)
4-(2-Diethylaminoethylamino)phenyl 4-nitrophenyl sulfide	(434)
Di-n-hexadecyl sulfide	(457)
2,2'-Dihydroxydiethyl sulfide (thiodiglycol)	(330, 421)
Di-(p-methoxyphenyl) sulfide	(457)
4-(2,5-Dimethyl-1-pyrryl)diphenyl sulfide	(229)
2,2'-Dimethylsulfonyldiethyl sulfide	(154)
2,2'-Dimethylthiodiethyl sulfide	(154, 168, 342)
1,2-Dimethylthioethane	(154, 168)
2,2'-Di(2-methylthioethylthio)diethyl ether	(342)
2,2'-Di(2-methylthioethylthio)diethyl sulfide	(342)
1,2-Di(2-methylthioethylthio)ethane	(342)
Di(p-nitrobenzyl) sulfide	(457)
Di(nitro-tert-butyl) sulfide	(245a)
Di(2-nitro-1-methylpropyl) sulfide	(245a)
2,8-Dinitro-10-methylthiaxanthenol	(6)
2,8-Dinitrothiaxanthone	(6)
Diphenyl disulfide	(266)
Di(2-phenylethyl) sulfide	(457)
Diphenylmethyl α-naphthyl sulfide	(300)
Diphenylmethyl phenyl sulfide	(300)
Diphenyl sulfide	(87, 328, 329, 457)
Di(β-pyridiniummethyl) sulfide dichloride	(496)
Di(p-tolyl) sulfide	(457)
Divinyl sulfide	(330)
Dodecyl 2,3-dihydroxypropyl sulfide	(298)
Ethyl benzyl sulfide	(121)
Ethyl n-butyl sulfide	(228)
Ethyl chloromethyl sulfide	(121, 122)
Ethyl ethoxymethyl sulfide	(121)
Ethylene-sulfur chloride reaction product	(404)
Ethyl oleyl sulfide	(298)
8-Ethylthiocaffeine	(331b)
4-(2-Hydroxyethylthiol)-2-aminobutyric acid	(490)
2-Hydroxyethyl naphthenyl sulfides	(298)
4-Iodo-4'-nitrodiphenyl sulfide	(5)
2-Iodo-8-nitrothiaxanthene	(4a)
Methionine	(525)
6-Methoxy-8-(4-quinazolonyl)phenyl sulfide	(202)
2'-Methyl-4-aminodiphenyl sulfide	(229)
3'-Methyl-4-aminodiphenyl sulfide	(229)
4-Methyl-4-aminodiphenyl sulfide	(229)
Methyl 2-chloroethyl sulfide	(154, 155a)

TABLE 5—*Concluded*

SULFUR COMPOUND	REFERENCES
3'-Methyl-2,4-diaminodiphenyl sulfide	(229)
3'-Methyl-4-(2,5-dimethyl-1-pyrryl)diphenyl sulfide	(229)
4'-Methyl-4-(2,5-dimethyl-1-pyrryl)diphenyl sulfide	(229)
3'-Methyl-2,4-dinitrodiphenyl sulfide	(229)
2'-Methyl-2-nitrodiphenyl sulfide	(229)
2'-Methyl-4-nitrodiphenyl sulfide	(229)
3'-Methyl-4-nitrodiphenyl sulfide	(229)
4'-Methyl-4-nitrodiphenyl sulfide	(229)
Methyl 2-nitroethyl sulfide	(245a)
Methyl 2-nitropropyl sulfide	(245a)
8-Methylthiocaffeine	(331b)
Methyl p-tolyl sulfide	(228)
Mustard gas (Levinstein)	(223)
5-Nitro-2-(p-bromothiophenoxy)benzoic acid	(4a)
4-Nitrodiphenyl sulfide	(229)
5-Nitro-2-(p-iodothiophenoxy)benzoic acid	(4a)
6-Nitro-2-methylthioxanthene	(163a)
7-Nitro-2-methylthioxanthene	(163a)
6-Nitro-2-methylthioxanthone	(163a)
7-Nitro-2-methylthioxanthone	(163a)
5-Nitro-2-(p-nitrothiophenoxy)acetophenone	(6)
p-Nitrophenyl octyl sulfide	(159)
2-Nitro-4-(p-tolylthio)benzaldehyde	(163a)
4-Nitro-2-(p-tolylthio)benzaldehyde	(163a)
Phenyl 2-hydroxy-3-chloropropyl sulfide	(388)
Phenyl 2-hydroxycyclohexyl sulfide	(388)
Phenyl octyl sulfide	(159)
8-Phenylthiocaffeine	(331b)
2-Phenylthio-2'-methylthiodiethyl sulfide	(154)
1-Phenylthio-2-methylthioethane	(154, 168)
4'-Isopropyl-4-aminodiphenyl sulfide	(229)
4'-Isopropyl-2,4-dinitrodiphenyl sulfide	(229)
4'-Isopropyl-4-nitrodiphenyl sulfide	(229)
8-n-Propylthiocaffeine	(331b)
8-Isopropylthiocaffeine	(331b)
n-Propyl p tolyl sulfide	(228)
Pseudomethionine	(490)
2-Succinylamino-4'-nitro-5-thiazolylphenyl sulfide	(35)
Thianthrene	(116)
Thioxanthene	(265a)
Thioxanthone	(265a)
p-Tolyl 2-chloroethyl sulfide	(155a)
Vinyl thiocresyl ethers	(537)

nitrosobenzene (50 per cent) and azoxybenzene (35 per cent) by the oxidation of aniline in an aqueous system with peracetic acid added dropwise, but when the peracid is added in one portion, a 70 per cent yield of nitrosobenzene and a 25 per cent yield of azoxybenzene are obtained. In similar reactions (184, 189)

p-toluidine yields nitrosotoluene, azotoluene, and azoxytoluene; m- and p-nitro-anilines yield nitronitrosobenzene and dinitroazoxybenzene; and anthranilic acid in alcohol solution yields nitrosobenzoic acid. Recently Greenspan (232) obtained an 85 per cent yield of azoxybenzene and a 15 per cent yield of nitrobenzene from aniline by oxidation with 45 per cent peracetic acid. Azo compounds are presumably the precursors of the azoxy compounds.

Bigiavi (57) and Bigiavi and Albanese (60) reported that, unlike the free amino compounds, acetyl derivatives of simple primary aromatic amines are converted to nitro derivatives only. Compounds studied were the acetyl derivatives of aniline, p-bromoaniline, p-nitroaniline, p-toluidine, pseudocumidene, and isomeric p-aminoazobenzenes.

Gambarjan (225) obtained an orange-red compound, melting at 138–142°C., when diphenylamine was oxidized with perbenzoic acid.

2. Oxidation of azo compounds to azoxy compounds

One of the most clean-cut reactions of organic peracids is the conversion of azo compounds to azoxy compounds. This reaction proceeds readily under mild conditions, and quantitative yields are frequently obtained. In most cases, hydrogen peroxide and acetic acid have been employed, but in some, previously prepared peracetic acid has been used. This reaction was explored from 1910 through 1934 by Angeli, Bigiavi, D'Ans, and their coworkers. Azo compounds converted to azoxy compounds are listed alphabetically in table 6.

3. Oxidation of amines to amine oxides

Amine oxides can be prepared in good yields from amines by reaction with organic peracids. Monopersulfuric acid (Caro's acid) is not satisfactory for this reaction, and aqueous hydrogen peroxide reacts very slowly and gives low yields of N-oxide (347). Although organic peracids do not yield the N-oxide directly, and salts of the carboxylic acids are formed thereby requiring further processing, the N-oxides are usually purified more easily than when hydrogen peroxide alone is employed (42). Amines converted to N-oxides by oxidation with organic peracids (usually perbenzoic and monoperphthalic acids) are listed alphabetically in table 7.

D. OXIDATION OF ALDEHYDES

Aldehydes are usually converted to the corresponding acids in excellent yield by organic peracids (1, 31, 144, 163a, 189, 219, 332, 333, 440, 463, 511, 561, 570, 578). This oxidation reaction appears to be a general one, with the exception of the oxidation of phenolic and etherified phenolic aldehydes.

Phenolic aldehydes, as well as etherified phenolic aldehydes, undergo a more complex reaction, in which the aldehyde group is converted to the phenolic hydroxyl group (or the acylated hydroxyl group). This reaction appears to have been discovered by Dakin (179), who obtained an abundant yield of catechol from o-hydroxybenzaldehyde on oxidation with perbenzoic acid. D'Ans and Kneip (189) showed that p-hydroxybenzaldehyde behaves similarly on oxidation

with peracetic acid, yielding hydroquinone and its oxidation products quinhydrone and quinone. Böeseken and coworkers (91, 97) oxidized various etherified phenolic aldehydes, and demonstrated that peracetic acid converts the aldehyde group to the phenolic hydroxyl group. Compounds studied were piperonal (91),

TABLE 6

Azo compounds converted to azoxy compounds by oxidation with organic peracids

AZO COMPOUND	REFERENCES
4-Acetoxyazobenzene	(9)
4-Acetylaminoazobenzene	(57, 59, 400)
4-Acetylazobenzene	(10)
4-Aminoazobenzene	(400, 540)
Azobenzene	(7, 189)
4-Benzoxyazobenzene	(58)
4-Benzoylazobenzene	(10)
4-Bromoazobenzene	(18)
p-Bromoazo-o-toluene	(19)
4-Bromohydrazobenzene	(9)
2-Bromo-4-nitroazobenzene	(61)
4-Bromo-4'-nitroazobenzene	(18)
4-Carboxyazobenzene	(20)
Cyanomethylazobenzene	(10)
4,4'-Diacetoxyazobenzene	(62)
Diazoresin (from aniline)	(17)
Dibenzoyl-o-azophenol	(67)
4,4'-Dibromoazobenzene	(18)
2,4-Dihydroxyazobenzene	(65)
2,5-Dihydroxyazobenzene (benzoyl and acetyl derivatives)	(64)
4,4'-Dihydroxyazobenzene	(9, 14, 62)
3,3'-Dinitroazobenzene	(189)
4,4'-Dinitroazobenzene	(189)
4-Hydroxyazobenzene	(58, 68)
2-Hydroxy-5-methylazobenzene	(69)
4-Methylazobenzene	(70)
4-Nitroazobenzene	(15, 16)
N,N'-Di-2-pyridyl-4,4'-hydrazobenzenedisulfonamide	(333a)
Phenylazocarboxamide	(12, 13)
Polyazo compounds	(8)
Quinone phenylhydrazones (benzoyl derivative)	(58)
4-Sulfoazobenzene	(20)
2,4,6-Trinitroazobenzene	(20)
2,3,4-Trihydroxyazobenzene (and tribenzoate)	(66)

3,4-dimethoxyvanillin (97), ethylvanillin (97), 3-ethoxy-4-methoxybenzaldehyde (97), 3,4-diethoxybenzaldehyde (97), 3-methoxy-4-butoxybenzaldehyde (97), and 3-ethoxy-4-butoxybenzaldehyde (97). Formic acid is also obtained as an oxidation product in these reactions, but its origin was not explained. Some years later, the reaction was studied further by von Wacek and coworkers (550, 550a, 551, 552), who showed that hydrogen peroxide–acetic acid, as well as preformed peracetic

TABLE 7
Amines converted to amine oxides by oxidation with organic peracids

AMINE	REFERENCES
4-*p*-Acetamidophenylsulfonylpyridine	(159)
Benzo-[*f*]-quinoline	(25)
7-Chloroisoquinoline	(461)
6-Chloroquinoline	(25)
Cinchonidine	(42)
Cinchonine	(42)
2,5-Di-*sec*-butylpyrazine	(390a)
Dihydrostrychnine	(307)
Dimethylaniline	(45a)
2,5-Dimethylpyrazine	(390a)
2,3-Diphenylquinoxaline	(331a, 336a)
Ethylallylaniline	(348a)
Ethylbis(2-chloroethyl)amine	(495)
1-Hydroxyphenazine	(171a)
Isoquinoline	(348)
6-Methoxy-8-acetylaminoquinoline	(230)
6-Methoxyisoquinoline	(461)
6-Methoxyquinoline	(541)
Methylallylaniline	(299a, 347)
2-Methyl-3-*n*-amylquinoxaline	(340a)
Methylbenzylaniline	(299a, 348a)
Methylbenzylaniline picrate	(299a)
Methylbis(2-chloroethyl)amine	(495)
Methylcinnamylaniline	(299a)
Methylcrotylaniline	(299a)
Methyldiethanolamine	(495)
Methyldiphenylamine	(45a)
2-Methyl-3-phenyl-1,2-naphthoquinoxaline	(336a)
2-Methylquinoxaline	(340a)
Neostrychnine	(166)
1,2-Naphthophenazine	(336a)
5-Nitroquinoline	(230, 560)
6-Nitroquinoline	(25)
o,m,p-Phenanthrolines	(295a, 331a)
Phenazine	(171a, 340a, 438a)
Pyridine	(348)
Quinaldine	(348b)
Quinidine	(42)
Quinine	(42)
Quinoline	(348)
Quinoxaline	(340a)
Strychnine	(307)
1,2,3,4-Tetrahydrophenazine	(340a)
2,4,6-Triphenylpyridine	(348)
Tris(2-chloroethyl)amine	(495)

acid, can be employed and that the reaction is also applicable to appropriately substituted aromatic ketones. Since formyl esters are obtained in a few of the

reactions (550, 550a), it was concluded that this product is an intermediate and on hydrolytic cleavage yields the phenol and formic acid. The reaction apparently involves the insertion of an oxygen atom between the carbon atom of the carbonyl group and the aromatic carbon atom to which it is attached, and is analogous to the reaction of peracids with α,β-unsaturated aliphatic ketones discussed earlier (100, 102, 113). Compounds oxidized by von Wacek and coworkers were salicyl-aldehyde (550, 550a, 551, 552), 6-hydroxy-3-methoxybenzaldehyde (550), 2-hy-droxy-4-methylbenzaldehyde (550), m- and p-hydroxybenzaldehydes (550), veratraldehyde (550), salicylaldehyde methyl ether (550), and p-methoxyaceto-phenone (550), the expected phenols being obtained generally in excellent yield. Anisaldehyde, however, is converted to anisic acid in good yield (189).

E. OXIDATION OF KETONES AND QUINONES

In general, monoketones are unaffected by organic peracids, but in a few cases, mostly cyclic and methyl ketones, oxidation has been reported. Baeyer and Villiger (31) obtained mentholactone from menthone, Burckhardt and Reich-stein (157, 158) converted some sterol ketones to lactones, and Sarett (477b) converted several methyl ketones of the pregnane series to acetoxy derivatives on oxidation with perbenzoic acid. This reaction is similar to the Baeyer oxida-tion of ketones with monopersulfuric acid (Caro's acid) (30). As mentioned before, however, p-methoxyacetophenone is converted to hydroquinone mono-methyl ether by peracetic acid (550).

Diketones and quinones are cleaved to carboxylic acids by organic peracids. Perkin (403) showed that hydrogen peroxide and acetic acid react readily with 1,2-diketones and with substances containing the quinonoid structure. Benzil and phenanthraquinone are converted to benzoic and diphenic acids, respectively (403). Aurine yields p-hydroxybenzoic acid and hydroquinone, the latter being oxidized to benzoquinone (403). Brazilein and trimethylbrazilein yield acids having the formulas $C_{16}H_{14}O_9$ and $C_{19}H_{20}O_8$, respectively (403). Charrier and Beretta (169) oxidized acenaphthenequinone and phenanthraquinone to diphenic acids, β-naphthoquinone to phthalic acid, and 2-N-phenyl-1,2-naphthotriazole-quinone and 2-N-p-chlorophenyl-1,2-naphthotriazolequinone to the anticipated dibasic acids with hydrogen peroxide–acetic acid. Böeseken and Slooff (108), however obtained o-carboxyallocinnamic acid by oxidizing β-naphthoquinone with peracetic acid, and Karrer and Schneider (291) obtained a similar result with perbenzoic acid. o-Benzoquinone is similarly cleaved, yielding cis,cis-muconic acid (107, 108), and on oxidation with monoperphthalic acid in ether solution, tetrabromo-o-quinone yields the lactone of tribromomucic acid (291).

On oxidation with peracetic acid, 9,10-diketostearic acid is quantitatively converted to azelaic and pelargonic acids (108). Diacetyl and benzil behave similarly, yielding acetic and benzoic acids, respectively. In the oxidation of the 1,2-diketone ($[C_6H_5(CH=CH)_2CO]_2$) with monoperphthalic acid, Karrer and coworkers (282) obtained a product ($C_{22}H_{18}O_3$) whose structure was not estab-lished and a small quantity of 5-phenylpentadienoic acid.

1,3-Diketones are also cleaved by peracetic acid (101), yielding an acid and an

alcohol in the absence of excess peracetic acid, and 2 moles of acid when an excess of peracetic acid is employed. 1,3-Diketones having the group —COCH₂CO— are more easily oxidized than the monosubstituted diketones —COCHRCO—. Diketones of the general formula RCOCHR'COR", in which R is methyl, ethyl, amyl, phenyl, or p-nitrophenyl, R' is hydrogen, methyl, or benzyl, and R" is methyl, methoxyl, or ethoxyl have been studied by Böeseken and Slooff (101). These workers concluded that the reaction involves enol formation first, followed by addition of oxygen at the double bond, yielding an oxirane compound. This then undergoes ring opening, with shifting of the group R', followed by hydrolysis or acetolysis (82).

F. OXIDATION OF ORGANIC IODINE COMPOUNDS

Organic iodine compounds when treated with peracetic acid usually yield diacetates of the corresponding iodoso compounds, whereas with perbenzoic acid iodoxy compounds are usually obtained (105, 106). On treatment with perbenzoic acid, the iodosoacetates are converted to iodoxy compounds. Böeseken and Schneider (104, 105, 106) obtained diacetates of the corresponding iodoso compounds by the oxidation of iodobenzene (104, 105, 106), diiodobenzenes (105, 106), iodotoluenes (105, 106), iodobenzoic acids (105, 106, 119), iodobenzene-sulfonic acids (105), o- and m-iodonitrobenzenes (105, 106), and 1,2-diiodo-ethylene (105) with peracetic acid. When perbenzoic acid is used as the oxidizing agent, the iodoxy compounds are obtained, with the exception of o-iodobenzoic acid and p-iodobenzenesulfonic acid, which yield iodoso compounds (105). Mono- and di-iodofumaric acids and iodoacrylic acid yield the iodoso compounds (106), iodoform is converted to iodine and iodine pentoxide, and diiodoacetylene is converted to tetraiodoethylene (106). Surprisingly, on oxidation with peracetic acid in chloroform solution 1,2-diiodo-1,2-diphenylethylene (1,2-diiodostilbene) yields 1,2-dichloro-1,2-diphenyl-1,2-epoxyethane (1,2-dichlorostilbene oxide), thus indicating that the solvent may play a role in some peracid oxidations (106).

The oxidation of iodobenzene with peracetic acid has also been studied by Arbuzow (21), who demonstrated that with dilute peracetic acid good yields of the diacetate of iodosobenzene are obtained but with 90 per cent peracetic acid in ether solution mixtures of iodoxybenzene and of the diacetate of iodosobenzene are obtained. By employing 50 per cent peracetic acid and sodium bicarbonate in the reaction, iodoxybenzene is obtained. With perbenzoic acid, iodobenzene yields the benzoyl derivative of iodosobenzene (21). When iodoxybenzene is treated with 50 per cent peracetic acid, the diacetate of iodosobenzene is obtained (21).

Jorissen and Dekking studied the oxidation of iodobenzene dissolved in acetaldehyde (277) or in benzaldehyde (276) through which oxygen was being passed. Peracetic or perbenzoic acid (prepared and utilized *in situ*) was assumed to be the oxidizing agent. In acetaldehyde solution iodoxybenzene was obtained, whereas in benzaldehyde solution iodosobenzene was obtained. These results are not in accord with the results of Böeseken and Schneider (105, 106).

G. MISCELLANEOUS

The oxidation of thiopyrine to the trioxide by peracetic acid has been reported by D'Ans and Kneip (189), although the structure of the product was not given. Arbuzow (21) oxidized diphenylselenide with peracetic acid in ether and also in acetic acid solution. With dilute peracetic acid, the hydrate of diphenylselenoxide as well as its monoacetate was obtained, and with 90 per cent peracetic acid, diphenylselenone was obtained. With perbenzoic acid in ether solution, diphenylselenide was converted to diphenylselenone (21). Yields in these reactions were good. Triphenylphosphine oxide was also obtained in good yield by the oxidation of triphenylphosphine with dilute peracetic acid (21).

Medvedev and Alekseeva (344) oxidized hexaphenylethane with perbenzoic acid and obtained triphenylmethylperoxide and two isomers of the formula $C_{38}H_{30}O$, one of them being $(C_6H_5)_2C(OC_6H_5)C(C_6H_5)_3$.

By oxidizing several carbenium perchlorates with hydrogen peroxide and acetic acid Dilthey, Quint, and Dierichs (193) obtained cleavage of carbon-to-carbon bonds, with the formation of ketones and phenols.

The action of perbenzoic acid on numerous polycyclic aromatic compounds was studied by Eckhardt (198), who reported that methylcholanthrene and 3,4-benzopyrene absorb oxygen most rapidly. Other compounds studied were pyrene, benzopyrene-5-aldehyde, 5-nitrobenzopyrene, 4- and 6-methyl-1,2-benzanthracenes, 1,2-benzanthracene, 1,2,5,6-dibenzanthracene, and anthracene. Oxidation products were not reported. Wittig and Henkel (575) observed that a large excess of perbenzoic acid converts 9,10-diphenylacenaphthylene to 1,8-dibenzoylnaphthalene.

Karrer and Tragenberger (293) oxidized the methyl ether of 3,7,4'-trimethoxy-2-phenylbenzopyrylium base with monoperphthalic acid and obtained 7,4'-dimethoxyflavonol. A complex reaction involving oxidation at the double bond as well as loss of methoxyl occurs.

Under certain conditions, polyhydric phenols are oxidized to quinones by organic peracids. Excesses of peracid must be avoided since, as mentioned earlier (Section III, E), it will attack the quinone further, yielding carboxylic acids. Perkin (403) observed that hydroquinone yields benzoquinone, and Bigiavi and de Benedetti (64) reported that benzeneazohydroquinone yields the corresponding quinone when hydrogen peroxide–acetic acid is employed as the oxidizing agent. Pratesi and Celeghini (419) reported that 2,5-bis[2,4-dimethyl-N-pyrryl]-3,6-dibromohydroquinone is converted to an intensely blue quinone by oxidation with perbenzoic and monoperphthalic acids, or with peroxides, such as ethyl, benzoyl, and hydrogen peroxide. In the oxidation of pyrogallol with percompounds, in the presence of peroxides, Wieland and Sutter (572) and Böeseken (82) reported that disubstituted peroxides have no effect but that peracetic and perbenzoic acids cause oxidation to occur. Products were not isolated.

An unusual reaction is the dehydrogenation of isopyrocalciferol acetate to dehydroergosterol acetate by perbenzoic acid (573a).

Tri-n-butylborine is quantitatively oxidized by perbenzoic acid, yielding n-butyl alcohol and boric acid (275).

In the thiaxanthene series, the reactive methylene group can be converted to the carbonyl group by oxidation with hydrogen peroxide and acetic acid (4a, 163a, 265a).

Attention is directed to the brief review on oxidations with organic peracids by Böeseken (81).

IV. ORGANIC PERACIDS IN THE DETERMINATION OF STRUCTURE AND IN THE ANALYSIS OF ORGANIC COMPOUNDS

The reaction of organic peracids with organic compounds has been employed by many investigators to determine the number of atoms of oxygen consumed per mole of organic compound. This technique has been employed either as an analytical tool or, in the determination of structure, as an additional method for confirming the presence of an oxidizable group, such as the double bond, in the molecule. The usual procedure is to add a measured quantity of a solution of the organic peracid of known concentration to the compound being studied and follow the disappearance of the peracid iodimetrically. In describing their results, some investigators have reported the number of atoms of oxygen consumed per mole of compound oxidized; others have converted oxygen consumption data to iodine numbers; and others have preferred the term "oxygen number" (378) (defined as the amount of active oxygen, supplied by perbenzoic acid, required for the oxidation of 100 g. of the substance). When pure compounds are being studied, the oxygen consumption should be reported as the number of atoms of oxygen consumed per mole of compound oxidized. Most of the investigators who have merely studied the analytical aspects of organic peracid oxidations have not isolated the oxidation products. Likewise, many of the investigators who have studied reactions with organic peracids as a preparative tool have not been concerned with the quantitative aspects of the reaction from the analytical standpoint, such as optimum times and temperatures of reaction and excess of reagent required.

An alphabetical list of substances which have been treated with organic per-acids for the purpose of measuring oxygen consumption is given in table 8. In many of the cases listed quantitative reaction occurs, and the results are of considerable value, but in others insufficient reaction time has been allowed or side reactions occur, so that the data on oxygen consumption do not give a true picture of the structure of the substance. Some of the substances appear in previous tables if oxidation products have been isolated.

Determination of the total number of double bonds in olefins by peracid analysis is not so satisfactory as quantitative catalytic hydrogenation or even determination of iodine or bromine number, since oxygen consumption may be incomplete or unusually high oxygen absorption may occur as a result of side reactions with other functional groups. Determination of the rate of reaction of peracids with unsaturated compounds, particularly hydrocarbons, however, yields much reliable information regarding their structure, and this technique may become a valuable tool in structure elucidation (302, 304, 476a, 553, and Section V).

TABLE 8

Substances for which oxygen consumption measurements have been reported

SUBSTANCE	REFERENCES
Abietic acid	(357, 470)
Agnosteryl acetate	(574a)
Allyl alcohol	(360)
Amyrilene	(470, 473)
Amyrins	(473)
Anethole	(74, 357)
Anthracene	(198)
dl-Alanine	(525)
l-Arginine	(525)
dl-Aspartic acid	(525)
Atisine	(267a)
Benzalacetophenone	(580)
Benzaldehyde	(511)
Benzine	(378)
3,4-Benzopyrene	(198)
Benzopyrene-5-aldehyde	(198)
Benzoylacetone	(75)
Benzylideneglycine (barium salt)	(128)
Benzoylacetone	(128)
Bixin	(437)
Bornylene	(346, 380)
Camphene	(346)
Carotene	(436)
Carvone	(267a)
Castor oil	(488)
Chloromethyl ethyl sulfide	(122)
Chloromethyl methyl sulfide	(122)
Chloromethyl propyl sulfide	(122)
Cholesterol	(357, 360)
Cinnamalacetone	(580)
Cinnamic acid	(357)
Cinnamic aldehyde	(357)
Cinnamyl alcohol	(122)
α-Cinnamylideneacetophenone	(249)
α-Cinnamylideneacetophenone oxide	(249)
Citral	(74)
Citronellol	(74, 357, 360)
Cocoa butter	(124)
Crotonaldehyde	(580)
Crotonic acid	(357)
Cyclofenchene	(380)
Cyclohexene	(267a)
Cystine	(525)
Dehydroandrosterone	(191)
Diallyl sulfide	(122)
1,1-Dianisylethylene	(346)
Dibenzalacetone	(580)
1,2,5,6-Dibenzanthracene	(198)
Dibenzoylmethane	(75)

TABLE 8—*Continued*

SUBSTANCE	REFERENCES
Dibenzyl sulfide	(122)
Dibenzyl sulfoxide	(122)
Diethylamine	(128)
Dihydroagnosteryl acetates (α and β)	(574a)
Dihydroamyrilene	(473)
α-Dihydrolanosteryl acetate	(574a)
p-Dimethylaminoazobenzene	(11)
Dimethylcinnamylidenemalonate	(249)
Dimethyldihydroresorcinol	(128)
2,6-Dimethyl-6-octene	(511)
2,4-Dimethyl-2-pentene	(357)
1,1-Diphenylethylene	(346)
Diphenyloctatetraene	(437)
Dithioglycolic acid	(525a)
Elaidic acid	(99, 124)
α-Elemolic acid	(472b)
α-Ergostenol acetate	(574)
Ergosterol	(357, 360)
Ethyl acetoacetate	(75, 128)
Ethylamine	(128)
Ethyl benzyl sulfoxide	(122)
Ethyl eleostearate	(99)
Ethylideneacetone	(580)
Ethyl 9,12-octadecadienoate (linoleate)	(39)
Ethyl 9,12,15-octadecatrienoate (linolenate)	(488)
Ethyl oleate	(37, 39)
N-Ethylpiperidine	(267a)
Ethylthioglycolic acid	(122)
Eugenol	(74, 346)
1-α-Fenchene	(346)
Furoic acid	(360)
Geraniol	(74, 360)
Geranyl acetate	(74)
l-Glutamic acid	(525)
Glycine	(525)
Glycine anhydride dibenzyl ether	(128)
Guanidine carbonate	(128)
Hendecenoic (undecylenic) acid	(302, 476a)
1-Heptenal	(511)
2,4-Hexadiene	(357)
l-Histidine	(525)
Histidine dihydrochloride	(128, 129)
l-Hydroxyproline	(525)
Imidazole	(129)
β-Ionone	(580)
Isoatisine	(267a)
d-Isoleucine	(525)
l-Isoleucine	(525)
Isoprene	(437, 456)

TABLE 8—*Continued*

SUBSTANCE	REFERENCES
Isoeugenol	(74, 122, 346, 357, 360)
Isosafrole	(346, 357, 360)
Kerosene	(378)
Lanostenones	(195)
Lanosterols	(195, 197, 574a)
Lanosteryl acetate	(192)
l-Leucine	(525)
Limonene	(346, 357, 360, 380, 456)
Linseed oil	(124, 488)
Lubricating oils	(378)
Lycopene	(437, 456)
Lysidine	(129)
l-Lysine	(525)
Menthene	(380, 511)
8-Menthene-1,2-diol	(346)
Mesityl oxide	(357)
dl-Methionine	(525)
Methyl 3(α)-acetoxy-9-hydroxy-Δ^{11}-cholenate	(261)
4-Methyl-1,2-benzanthracene	(198)
6-Methyl-1,2-benzanthracene	(198)
α-Methylcamphene	(380)
Methylcholanthrene	(198)
Methyl cinnamylideneacetate	(249)
1-Methyl-2,2-diphenylethylene	(346)
Methyl elaidate	(99)
Methyl α-elemolate	(472b)
2-Methylimidazole	(129)
Methyl 9,12,15-octadecatrienoate (linolenate)	(99)
Methyl pimarate	(475)
Methyl piperate	(249)
5-Nitrobenzopyrene	(198)
Nonene	(357)
Octadecadienoic (linoleic) acids	(39, 99, 124, 357, 488)
Octadecatrienoic acid	(37)
Oil of calamus	(74)
Oil of caraway	(74)
Oil of cinnamon	(74)
Oil of citronella	(74)
Oil of clove	(74)
Oil of fennel	(74)
Oil of lavender	(74)
Oil of thyme	(74)
Oleic acid	(37, 39, 124, 302, 357, 476a, 488)
Olive oil	(124, 488)
Oxoisoatisine	(267a)

TABLE 8—*Concluded*

SUBSTANCE	REFERENCES
Petrolatum...	(378)
dl-Phenylalanine	(525)
1-Phenyl-1-anisylethylene	(346)
α-Pimaric acid	(470)
Pinene	(122, 346, 357, 360)
Poppyseed oil...	(122)
Polystyrene...	(338a)
l-Proline	(525)
Pyrene	(198)
Pyrotartaric acid	(75)
Rubber (natural)...	(304, 436, 476a, 553)
Rubber (synthetic)	(304, 476a, 553)
Rapeseed oil	(488)
Safflowerseed oil	(488)
Safrole	(346, 360)
d-Serine...	(525)
dl-Serine	(525)
Sesame-seed oil	(124)
Sorbic acid, esters, amide, and chloride	(249)
Soybean oil	(488)
Styrene	(511)
α-Terpineol	(346)
Tetrahydroabietic acid	(470)
Tetrahydroatisine...	(267a)
Tetramethylethylene	(360)
dl-Threonine	(525)
Tricyclene	(380)
3,4,5-Trimethyloxazole	(128)
Triolein	(124)
l-Tryptophan	(525)
l-Tyrosine...	(525)
Uric acid (potassium salt)...	(128)
dl-Valine	(525)
Xanthophyll..	(437)

V. KINETICS, MECHANISM, AND ELECTRONIC INTERPRETATION OF THE OXIDIZING ACTION OF ORGANIC PERACIDS

Most of the discussion in this section will be devoted to the peracid oxidation of olefins, since more study has been devoted to olefins than to any other class of organic compounds oxidized with organic peracids, particularly from the standpoint of reaction kinetics.

The first systematic and reasonably complete interpretation of the reaction of olefinic compounds with organic peracids in the light of modern electronic concepts was recently published by Swern (501). This investigator compiled a list of specific reaction rates (k) for the reaction of aliphatic, alicyclic, and aromatic olefinic compounds with peracetic acid in acetic acid solution and with perbenzoic acid in chloroform or carbon tetrachloride solution. These data, together with additional data, are shown in tables 9, 10, and 11.

TABLE 9

Specific reaction rates (k) for the reaction of aliphatic and alicyclic olefins with peracetic acid in acetic acid solution

OLEFIN	t	$k \times 10^3$ *	REFERENCES
	°C.		
Ethylene	25.8	0.19	(114, 115, 499)
Propylene	25.8	4.2	(114, 115, 499)
1-Pentene	25.8	4.3	(114, 115, 499)
1-Pentene	40.9	17.7	(115)
1-Hexene	25.8–26.2	4.9–5.1	(114)
1,5-Hexadiene	25.8	8.0	(115)
1-Heptene	25.8	5.5	(115)
1-Octene	25	5.0	(506)
1-Decene	25	4.7	(506)
Methyl hendecenoate	25	4.1	(217)
2-Methyl-1-propene	25.8	92	(114, 115, 499)
2-Methyl-1-propene	39.9	300	(115)
2-Butene	25.8	93	(115, 499)
2-Pentene	25.8	93–95	(114, 115, 499)
2-Pentene	40.0	309	(115)
2-Hexene	25.8–26.2	99–102	(114, 115, 500)
2-Hexene	41.0	342	(115)
3-Hexene	25.8–26.2	129–134	(114, 115, 500)
3-Hexene	41.0	457	(115)
3-Heptene	25.8	110	(98)
4-Nonene	25.8	105	(98)
Oleic acid	18	36	(111, 487)
Elaidic acid	18	23	(111, 487)
Ricinoleic acid	18	26	(111, 487)
Ricinelaidic acid	18	16	(111, 487)
2-Methyl-2-butene	25.8–26.4	980–1240	(114, 115, 499)
2-Methyl-2-butene	40.8	3000	(115)
Cyclobutene	25.8–26.4	20–22	(114, 115, 500)
Cyclobutene	40.1	60.4	(115)
Cyclopentene	25.8	185–195	(114, 115, 499)
Cyclopentene	39.6	526	(115)
Cyclohexene	15.2	49	(115)
Cyclohexene	25.8	129	(98, 114, 115, 499)
Cyclohexene	39.6	404	(115)
Cycloheptene	25.8	175	(98)
Cycloheptene	39.8	610	(98)
1-Methylcyclopentene	25.8	2220	(114, 115, 499)
1-Methylcyclopentene	40.9	6660	(115)

* Time in minutes; concentration in moles per liter.

On the basis of the electron-releasing and electron-attracting effects of groups attached to or in close proximity to the double bond, and their influence on the nucleophilic properties of the double bond, coupled with the assumption that the peroxide oxygen in organic peracids is electrophilic, a rational explanation was

offered (501) for the marked difference in specific reaction rates of most of the olefinic compounds reported in tables 9, 10, and 11. In addition, explanations were offered for the following facts: (a) The reaction of olefins with organic peracids is either slowed down considerably or does not take place at all when carboxyl, carboalkoxy, aldehydo, or keto groups are attached to or are in close proximity to the double bond (75, 431), as is the case in cinnamic (84, 92), sorbic (248, 249, 250), maleic (83, 84), fumaric (84), and crotonic acids (84, 135, 136) and their esters, imidazoledicarboxylic acids (129), allylmalonic acids (103), and 2-pentenoic and 2-hexenoic acids (137); (b) aliphatic monoölefins react slowly (217, 499, 500, 506), whereas substitution of the hydrogen atoms attached to the double bond by alkyl groups increases the reaction rate considerably (98, 114, 115, 499, 500), and phenyl groups usually have only a mildly accelerating effect (89, 96, 499); and (c) in the oxidation of isoprene, the ethylenic group to which the methyl group is attached is attacked first (86, 438), in the oxidation of

TABLE 10

Specific reaction rates (k) for the reaction of aliphatic and alicyclic olefins with perbenzoic acid

OLEFIN	t	$k \times 10^3$ [*]	REFERENCES
	°C.		
Sorbic acid (and alkyl sorbates)..	0	0.03–0.05	(249)
Sorbic acid (and alkyl sorbates).................	20	0.2	(249)
Sorbamide..........................	0	0.07	(249)
Sorbamide....	20	0.45	(249)
Crotonaldehyde..	20	0.76	(75)
Sorbyl chloride	0	0.23	(249)
Sorbyl chloride.	20	1.52	(249)
Hendecenoic (undecylenic) acid	0	16	(302)
$\Delta^{3,9}$-Menthene-1,2-diol	0	34.7	(346)
Camphene.......................	0	93.1	(346)
Oleic acid................	0	384	(302)
Pinene...................	0	1081	(346)

[*] Time in minutes; concentration in moles per liter.

2-methyl-2,3-butadiene (a substituted allene), geraniol, linalyl acetate, and citral, the ethylenic group to which two methyl groups are attached is attacked first (86, 431), and in the oxidation of methyl 2,4-hexadienoate (sorbate), the ethylenic group farther from the carbomethoxy group is attacked first (248, 250). Additional information on the influence of substituent groups on specific reaction rates has recently been reported by Heinänen (249).

Performic acid, however, behaves somewhat differently from other organic peracids. This oxidant reacts rapidly with compounds containing one as well as two electron-releasing groups (505, 506), whereas a slow reaction would be expected with the former class of compounds (501).

It is generally accepted that the reaction of organic peracids with olefins is of the second order, although Muskat and Herman (375) have reported that the perbenzoic acid oxidation of the methylstyrylcarbinols is a third-order reaction. Furthermore, the addition of oxygen at the double bond probably takes place

TABLE 11

Specific reaction rates (k) for the reaction of olefins containing aromatic groups with peracetic acid in acetic acid solution and with perbenzoic acid in chloroform or carbon tetrachloride solution

OLEFIN	PERACETIC ACID			PERBENZOIC ACID		
	t	$k \times 10^{5*}$	References	t	$k \times 10^{5*}$	References
	°C.			°C.		
Allylbenzene	25.8–26.1	1.9–2.0	(114, 115, 499)	25–30	6–15	(89)
Allylbenzene	39 6	7.4	(115)			
Stilbene	25.8–26.3	5.1–6.7	(114, 115, 499)	0–1	1–2	(89)
Stilbene	39.6	16.7	(115)	15–16	4	(89)
Stilbene				25–30	18	(89)
Isostilbene	25.8	11.1	(115, 499)	0–1	2	(89)
Isostilbene				15–16	9	(89)
Styrene	25.8	11.3	(114, 115, 499)	0–1	2–3.6	(89)
Styrene	40.8	34.4	(115)	15–16	8–25	(89)
Styrene				25–30	35	(89)
1-Phenyl-1-propene	25.8	46	(114, 115, 499)	0–1	3–15	(89)
1-Phenyl-1-propene	40.8	166	(115)	15–16	23–54	(89)
1-Phenyl-1-propene				25–30	110–190	(89)
Indene	25.8	47	(114, 115, 499)			
Indene	41.0	166	(115)			
1,1-Diphenylethylene	25.8	48	(114, 115, 499)			
1,1-Diphenylethylene	39.8	163	(115)			
1,4-Dihydronaphthalene	25.8	37	(114, 115, 499)			
1,4-Dihydronaphthalene	40.9	162	(115)			
1,2-Dihydronaphthalene	16.3	116	(115)			
1,2-Dihydronaphthalene	25.8	230–240	(114, 115, 499)			
1,2-Dihydronaphthalene	40.9	657	(115)			
Triphenylethylene	25.8–26.1	5.76	(114, 115)			
Triphenylethylene	41.2	19.5	(115)			
Methylindene	26.1	599	(115)			
Methylcinnamylideneacetone				0	0.01	(249)
1-Phenyl-2-acetylethylene				20	2.5	(75)
Cinnamic acid (and alkyl cinnamates)				20	0.13	(75)
Cinnamaldehyde				20	4.7	(75)
Cinnamyl alcohol				20	202.5	(75)
1-Phenyl-3-butene				15–16	8–9	(89)
1-Phenyl-2-butene				15–16	10	(89)
1-Phenyl-1-butene				15–16	80	(89)
Eugenol				0	2.2	(346)
Isoeugenol				0	127	(346)
Safrole				0	1.3	(346)
Isosafrole				0	148	(346)
1,1-Diphenyl-1-propene				0	17.7	(346)

* Time in minutes; concentration in moles per liter.

by a *cis*-addition mechanism (24, 135, 296, 502), and the initial product of oxidation is the oxirane compound, which may or may not be the product isolated,

depending on the reaction conditions (217, 501). On hydrolysis of the oxirane ring, with either acids or alkalies, a Walden inversion occurs (309a, 502).

By the application of the principles elaborated by Swern (501), it is possible to predict with a considerable degree of accuracy, especially in the aliphatic series, the specific reaction rate of the peracetic acid oxidation of an olefin of known structure, and suitable and safe reaction conditions can be readily devised. In addition, valuable information regarding the structure of an olefin may be obtained by determining its specific reaction rate with peracids. Also, a determination of the specific reaction rate of a mixture of olefins such as those obtained from dehydration, dehalogenation, dehydrohalogenation, and olefin polymerization reactions yields much information regarding the positions of the double bonds. An analytical method for the determination of "internal" and "external" double bonds in synthetic as well as natural rubbers, based on the rate of reaction of perbenzoic acid with the substance for a definite period of time, and comparison of the quantity of perbenzoic acid consumed with that of known mixtures of model compounds such as oleic and undecylenic acid, has been described by Kolthoff and coworkers (302, 304), Saffer and Johnson (476a), and Weidlein (553).

Only a limited number of kinetic data are available on the oxidation of other types of organic compounds with organic peracids (87, 116, 119, 333, 545), and therefore it is impossible to generalize regarding the mechanism of such oxidations. Furthermore, in some cases the occurrence of secondary reactions has obscured the interpretation of the results. Insofar as reliable information has been accumulated, these oxidations also support the assumption that the peroxide oxygen in organic peracids is electrophilic and is readily released in the presence of nucleophilic substances (501). The observation of Botvinnik (127) that perbenzoic acid reacts with ammonia and amines but not with their salts in which the nitrogen octet is apparently filled is also in line with this assumption.

The electronic structure of organic peracids is not known, but Wittig and coworkers (575, 577, 578) have made some interesting suggestions.

Medvedev and Blokh (345) have determined the rates of reaction of cyclohexene with peracetic, perbenzoic, p-methoxyperbenzoic, m- and p-nitroperbenzoic, and α- and β-pernaphthoic acids in benzene and xylene solutions and have reported that the nature of the solvent affects the speed of the reaction greatly, an observation made earlier by Meerwein and coworkers (346) and Lagrave (311). Kolthoff and coworkers (303) have suggested that chloroform be discouraged as a solvent for perbenzoic acid oxidations because of the high rate of decomposition of the peracid. The addition of 10 per cent of benzene to the chloroform, however, curtails the decomposition.

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Addendum[7]

Since December 1, 1947 other references dealing with organic peracids have come to our attention. These are given below in alphabetical order by the first author; the legend in parentheses after the date refers to the section of the present article in which the subject matter of the reference belongs. Of special interest are the papers by Byers and Hickinbottom, who have reported some abnormal reactions in the oxidation of diisobutylenes with organic peracids and are the first workers to have isolated an oxirane compound by the performic acid oxidation of an olefin. The direct perbenzoic acid oxidation of 2-pyridones to hydroxamic acids in 15–20 per cent yield has been reported by Lott and Shaw. Ross, Gebhart, and Gerecht have reported that performic acid oxidation of olefinic compounds having a hydroxyl group on a carbon atom directly adjacent to the olefinic group causes appreciable cleavage of the chain in addition to the expected hydroxylation reaction. Robinson and Waters, and Criegee, have suggested an ionic mechanism for the peracid oxidation of ketones; enolization is *not* the initial step, as had been suggested by Böeseken (82).

[7] Added May 20, 1949.

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THE STABILITY OF DETONATION

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CONTENTS

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FOREWORD

At the high temperature inside a detonating explosive the chemical reaction is much too fast to be studied directly (it is complete in perhaps one-millionth of a second). For a large class of phenomena this does not matter; all that needs to be known is the composition of the detonation products. With only this knowledge—and the aid of thermodynamic and hydrodynamic theory—we can find the detonation velocity itself, the pressure shock set up in air (or water, or earth), and the fragment velocities of a shell case.

But for another class of phenomena the chemical reaction is all-important: the conditions under which a high explosive may be detonated by a hammer blow or by another detonating explosive; the conditions under which a detonation will fail, and those under which it will build up to its full value; the comparison of unconfined with confined charges. All these involve the reaction rate.

The present paper is concerned with the theory of phenomena of this second class. It is in considerable measure a summary of theoretical studies by this research group, undertaken under the auspices of the Office of Scientific Research and Development and (in part) of the Bureau of Ordnance of the Navy Department.

In writing this paper, the authors have attempted:

(1) To simplify the mathematical derivations. With this in mind, every section of their earlier reports (OSRD 2026 and OSRD 3796) has been completely rewritten. Mathematical details which are off the main channel of the discussion have been relegated to appendices.

(2) To present the results in a form usable even without detailed study of the theory. To this end worked-out examples using representative data have been included regularly. No attempt has been made, however, to give encyclopedic coverage of all the experimental data on every topic.

(3) To make this as complete a manual in its part of the field of explosives as possible, by inclusion of theoretical treatments by various investigators and of many pertinent experimental results. In this connection it should be recognized that a considerable body of experimental fact and theoretical interpretation is as yet not available to the general public. Some other important work has not been published, although available in the form of unclassified reports.

Section I is a critical résumé of the classical theory of the detonation wave. In particular, the classical theory gives temperatures, pressures, and velocities within a detonating explosive.

Sections II B, II C, and II D contain the theories developed for detonation in finite charges, time-dependent detonation, and failure of detonation. These theories lead to the conclusions (Section II E) that the chemical reaction in a detonation starts at load-bearing contact points, proceeds only at the surfaces of grains, and is possibly diffusion-controlled.

Section III is a study of initiation by impact. A model is proposed whereby mechanical impact leads to internal burning, which goes over into detonation.

It is difficult under the present circumstances to give proper acknowledgment in every case for the benefits derived from discussion and conference with the many workers in this field, and for the considerable quantity of unpublished work which has contributed in large measure to the conclusions presented here. The authors are particularly indebted to Professor George B. Kistiakowsky for his discussions at the time this work was initiated and subsequently with him and Drs. Kirkwood, MacDougall, Messerly, and Boggs. These workers and others at the Explosives Research Laboratory at Bruceton made major contributions, both in experimental work and in the interpretation of the nature of explosives. Dr. Kistiakowsky asked the authors to explore the effects of charge diameter and finite reaction rates on the velocity of the explosion process. The prevailing opinion among the investigators in the field of explosives at that time was that kinetically the reaction in the detonation wave was identical with the process of deflagration of explosives and that the reaction was a heterogeneous one, starting at the surface of grains and extending into the gas phase. The development of this general idea and of the more specific arguments that arose from it proceeded in a coöperative manner among a large number of individuals and groups; under such circumstances any effort to establish priority is difficult, if not impossible, to achieve.

I. The Ideal Detonation Wave

A. FUNDAMENTAL THEORY

The discovery of detonation waves was made in 1881, independently by Berthelot and Vieille (8, 9) and by Mallard and Le Chatelier (52). Within twenty-five years of the discovery the fundamental theory of the detonation velocity in terms of thermodynamic and hydrodynamic properties had been correctly developed. Subsequent papers on the theory of detonation have chiefly been summaries of the results of the early writers (5, 7, 10, 41, 47, 51, 67, 75), detailed justifications of some of their assumptions, or numerical refinements in the application of their theory to actual explosives.

The development of the theory of the detonation velocity breaks naturally into two parts. The first part gives the relation between pressure and volume in a wave which propagates unchanged in type. In 1859 Earnshaw (25) obtained this relation correctly, but by a somewhat circuitous method. The still classic

researches of Riemann on sound waves (1860) went astray on this point, for he wrongly assumed the adiabatic relation $PV^\gamma =$ constant (61). Rankine (59) in 1870 gave a clear and correct derivation of the relation, but his work was overlooked by later workers. Hugoniot (39) independently (for he refers to no previous workers) rediscovered the relation (1887), and it was his presentation which was later utilized. The pressure–volume relation is now commonly linked with the names of both the latter men, and is called the Rankine–Hugoniot relation.

The second part of the theory of detonation velocity to be developed relates the detonation velocity to the sonic velocity behind the detonation wave. The earliest investigators give tentative explanations of the detonation velocity—thus Berthelot (8) (1881) thought that it was the mean kinetic velocity of the hot molecules, and Dixon (21) (1893) thought that it was the velocity of sound in the hot gases—but did not hit upon the correct explanation. Chapman (15) (1899) was the first to make the assumption now generally accepted, but his final results are somewhat in error since he followed Riemann's belief that the pressure–volume relation is adiabatic. Finally Jouguet (42) in 1905 independently made the same assumption, which is now generally called the Chapman–Jouguet condition. Jouguet made use of the Hugoniot relation, and with his investigation the fundamental hydrodynamic-thermodynamic theory reached its completion.

Both because the results of the hydrodynamic-thermodynamic theory are themselves interesting in giving a description of the structure of the detonation wave, and because the intermediate equations will be needed in later sections of this report, we shall here repeat the derivation of the fundamental theory.

As an idealization, consider a plane detonation wave propagating through a semi-infinite block of explosive. In front of the wave is the intact explosive (subscript zero); behind the wave are the products of explosion (subscript one). Separating these two regions is a "reaction zone" whose length we shall discuss presently. Now the explosive at the end of the reaction zone is described by these properties: the pressure P, specific volume (reciprocal density) V, the temperature T, the material velocity or velocity of flow W, and the detonation velocity D. To solve for all these properties, we use the following conditions:

(*1*) The equation of continuity or conservation of mass.[2]

$$\frac{dV}{dt} = V \frac{\partial W}{\partial x} \qquad\qquad \text{Mass} \quad (1a)$$

(*2*) The equation of motion or conservation of momentum.[2] Here the effects of viscosity are neglected.[3]

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[2] For three dimensions the equations of continuity and of motion are in the vector notation

$$\frac{dV}{dt} = V \operatorname{div} \vec{W}$$

$$\frac{dW}{dt} = -V\frac{\partial P}{\partial x} \qquad \text{Momentum} \quad (1b)$$

(3) The first law of thermodynamics, or law of conservation of energy. Any contribution of heat by thermal conduction is neglected,[3] although contribution of heat by chemical reaction is of course considered.

$$C_v dT = dE = dQ - PdV \qquad \text{Energy} \quad (1c)$$

(4) The assumption that the velocity and shape of the detonation wave do not change with time, whereupon we may choose a coördinate system in which the detonation wave is at rest in space and constant in time. In default of a rigorous a priori proof that such a steady detonation wave can exist, we shall use the fact that steady detonation waves are experimentally found.

If $y = Dt - x$ and $\tau = t$, then

$$\frac{\partial}{\partial \tau} = 0 \qquad \text{Steady state} \quad (1d)$$

(5) The Chapman–Jouguet condition, which says that the detonation velocity is the sum of the material velocity and the velocity of sound, both evaluated at the end of the reaction zone.[4]

$$D = W_1 + C_1$$

where

$$C_1 = V_0 \sqrt{-\left(\frac{\partial P}{\partial V}\right)_s} = V_0 \sqrt{-\gamma\left(\frac{\partial P}{\partial V}\right)_\tau} \qquad \text{Chapman–Jouguet} \quad (1e)$$

(6) The equation of state of the products of explosion. The one used here will be the simple Abel equation of state, with the covolume α assumed constant. The theory can be extended to more complicated equations of state without particular difficulty.[5]

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and

$$\frac{d\vec{W}}{dt} = -V \operatorname{grad} P$$

[3] See appendix A for a detailed discussion of the validity of neglecting viscosity and thermal conductivity.

[4] See appendix B for a detailed discussion of the validity of the Chapman–Jouguet condition.

[5] Cook, for example, uses the equation of state

$$P\{V - \alpha(V)\} = RT$$

while Halford, Kistiakowsky, and Wilson use an equation of the form

$$P(V - V_{\text{solids}}) = RT(1 + ze^{0.48})$$

where

$$x = \frac{k}{T^{0.25}(V - V_{\text{solids}})}$$

$$P(V - \alpha) = RT \qquad \text{State} \quad \text{(1f)}$$

Making use of the transformation of coördinates (equation 1d) and defining the material velocity in the new coördinate system as $U = D - W$, the three conservation equations take the following forms:

$$\frac{dV}{V} = \frac{dU}{U} \qquad \text{Mass} \quad \text{(2a)}$$

$$U dU = -V dP \qquad \text{Momentum} \quad \text{(2b)}$$

$$dE + P dV = dQ \qquad \text{Energy} \quad \text{(2c)}$$

and these combinations of the above:

$$\frac{D}{V_0} dU + dP = 0 \qquad \text{Mass + Momentum} \quad \text{(2d)}$$

$$dE + U dU + d(PV) = dQ \qquad \text{Energy + Momentum} \quad \text{(2e)}$$

Of these differential equations, equations 2a, 2d, and 2e can be integrated upon inspection, yielding:

$$\frac{V}{V_0} = \frac{U}{D} \qquad \text{(3a)}$$

$$P + \frac{U^2}{V} = P_0 + \frac{D^2}{V_0} \qquad \text{(3b)}$$

$$\Delta E + \tfrac{1}{2}U^2 + PV = \Delta Q + \tfrac{1}{2}D^2 + P_0 V_0 \qquad \text{(3c)}$$

and these combinations of the above

$$U^2 = V^2 \frac{P - P_0}{V_0 - V} \qquad \text{(4a)}$$

$$D^2 = V_0^2 \frac{P - P_0}{V_0 - V} \qquad \text{(4b)}$$

$$\Delta E = \Delta Q + \tfrac{1}{2}(P + P_0)(V_0 - V) \qquad \text{(4c)}$$

Also

$$\frac{P - P_0}{D^2} V_0 = \frac{W}{D} = 1 - \frac{V}{V_0} \qquad \text{(4d)}$$

and

$$(P - P_0)V_0 = WD \qquad \text{(4e)}$$

Either of the sets of equations 3 or 4 gives the results first obtained by Rankine and Hugoniot. Equation 4b gives the relation between P and V in all parts of a wave propagating at constant velocity D or, as the original investigators called it, "the condition for constancy of type." This is then the Rankine–Hugoniot adiabatic or "dynamic adiabatic" condition, and it will be seen that it makes P a linear function of V.

Some of the early investigators were troubled because the Rankine–Hugoniot adiabatic relation is not consistent with the ordinary adiabatic (i.e., isentropic) relation PV^γ = constant. Thus Rankine states: "No substance yet known fulfils the condition ... at a constant temperature, nor in a state of non-conduction of heat (called the adiabatic state)." Lamb (49), in his *Hydrodynamics*, repeats this statement and also remarks, "but no physical evidence is adduced in support of the proposed law." The explanation of this apparent difficulty is simple; the entropy is *not* constant in a shock or detonation wave, and there is accordingly no reason to expect the isentropic law to be followed. (In fact, the entropy exhibits a sharp increase at the front of detonation wave, and an additional increase throughout the reaction zone.)

Now equations 4 cannot be solved simultaneously to yield a unique value of D; an additional condition is needed, and this is the Chapman–Jouguet condition (equation 1e). When the sonic velocity is explicitly evaluated for equation of state (equation 1f),

$$U_1^2 = V_1^2 \gamma \frac{P_1}{V_1 - \alpha} \tag{5}$$

which when inserted into equations 4 gives at once the following results:[6]

$$\frac{V_1}{V_0} = \frac{\gamma + \alpha/V_0}{\gamma + 1} \tag{6a}$$

$$P_1(V_0 - \alpha) = 2R \frac{\Delta Q + \bar{C}_v T_0}{\bar{C}_v} \tag{6b}$$

$$T_1 = \frac{\Delta Q + \bar{C}_v T_0}{\bar{C}_v} \frac{2\gamma}{\gamma + 1} \tag{6c}$$

$$D^2 = (\Delta Q + \bar{C}_v T_0) \frac{2(\gamma^2 - 1)}{(1 + \alpha/V_0)^2} \tag{6d}$$

$$\frac{W_1}{D} = \frac{1 - \alpha/V_0}{\gamma + 1} \tag{6e}$$

B. APPLICATION OF FUNDAMENTAL THEORY TO ACTUAL EXPLOSIVES

Equations 6a to 6e furnish the detonation velocity and all properties of the explosion products with only four data: (*i*) the mean heat capacity of the products, (*ii*) the heat of explosion, (*iii*) the covolume, and (*iv*) the gas constant per gram. It is noteworthy that the *rate of chemical reaction* does not affect the detonation velocity or any of the properties of the products. (The properties at the shock front are likewise independent of the reaction rate; indeed, the properties at any point within the reaction zone are determined only by the extent of completion of the chemical reaction at that point, and not by the rate of chemical reaction.)

[6] These results are obtained by neglecting P_0, which is very small compared to P, in most problems of practical interest. However, the exact equations are assembled in appendix C.

Numerical refinement in the application of the fundamental theory has correspondingly taken three directions: (*i*) Accurate computation of the heat capacity at high temperatures and pressures, by the methods of statistical mechanics. (*ii*) Accurate evaluation of the heat of explosion, which requires first good calorimetric measurement of the heat of combustion, and secondly a calculation of the heat of explosion based on the composition of the explosion products, which supposes knowledge of chemical equilibria at high temperatures and pressures. A knowledge of the product composition also gives the mean molecular weight of the products, and thence the gas constant per gram. (*iii*) Theoretical prediction of the covolume to be used. Generally the fundamental theory is used in an inverted sense, to determine covolumes from the measured detonation velocities. But after enough explosives have been examined, it becomes possible to predict the covolume approximately from the final volume (Cook) or from the final volume, temperature, and composition (Halford, Kistiakowsky, and Wilson).

Summaries of the results of these numerical refinements will be found elsewhere.[7] For purposes of this report, high precision in these numbers is not essential, so we shall use the heats of explosion and heat capacities as tabulated by others, and find the covolume in the Abel equation of state by use of the known detonation velocities.

A single worked-out example will serve to illustrate the calculation. For TNT of density 1.57 we assume the data

$$V_0 = 0.6360 \text{ cm.}^3 \text{ g.}^{-1}$$

$$\bar{C}_v = 0.326 \text{ cal. deg.}^{-1} \text{ g.}^{-1}$$

$$\gamma = 1.240$$

$$D = 6.85 \times 10^5 \text{ cm. sec.}^{-1}$$

$$\Delta Q = 1080 \text{ cal. g.}^{-1}$$

$$R = \frac{82.07}{25.9} = 3.17 \text{ cm.}^3 \text{ atm. deg.}^{-1} \text{ g.}^{-1}$$

and find

$$\alpha = 0.4225 \text{ cm.}^3 \text{ g.}^{-1}$$

$$V_1 = 0.54 \text{ cm.}^3 \text{ g.}^{-1}$$

$$P_1 = 109,000 \text{ atm.}$$

$$T_1 = 3870°\text{K.}$$

$$W_1/D = 0.15$$

A word as to the probable accuracy of the properties predicted by the thermodynamic-hydrodynamic theory: (*1*) The temperature T_1 depends only on the

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[7] A series of papers by A. Schmidt (33). Also unpublished work of Cook, Kistiakowsky, Brinkley, Wilcox, and others.

heat ΔQ and the heat capacity $\bar{C}_v$, and in particular is independent of the co-volume or the initial density (except insofar as changes in final pressure may have a small effect on ΔQ and $\bar{C}_v$); the temperature should thus be the most accurately known property. (2) The ratios V_1/V_0 and W_1/D depend chiefly on the covolume α, which is not known with great certainty, so these are less accurate. (3) The velocity D involves all three data ΔQ, $\bar{C}_v$, and α, and so would be less certain than the preceding properties. (4) The pressure P_1 involves all three data and also the gas constant R per gram, which requires knowledge of the molecular weight of the products; this added uncertainty makes the pressure the least reliable of the predictable properties.
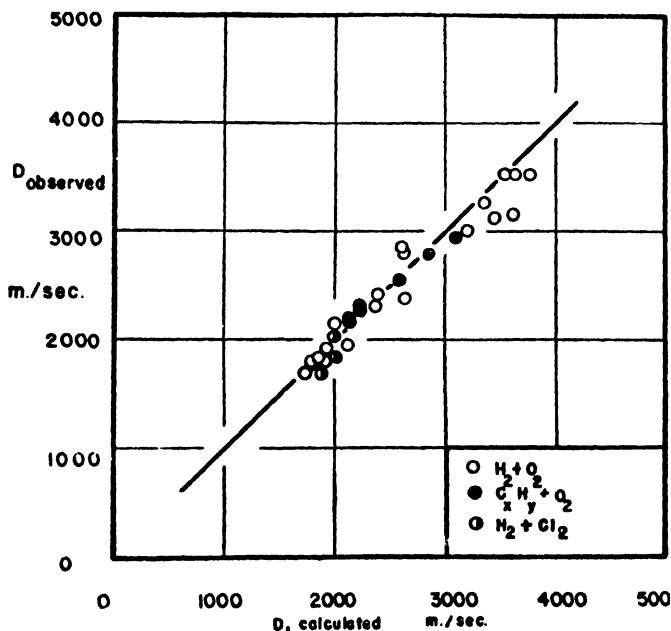
FIG. 1. Theoretical and calculated detonation velocities

Inspection of equations 6b and 6c shows that the temperature T_1 is only about 10 per cent higher than it would be if the reaction occurred at rest and at constant volume, while the pressure P_1 is precisely twice what it would be if the reaction occurred at rest and at constant volume.

C. DIRECT EXPERIMENTAL VERIFICATION OF THE FUNDAMENTAL THEORY

One test of the correctness of the hydrodynamic-thermodynamic theory lies in its ability to predict correctly the detonation velocities for gaseous explosives, since for these the covolumes are unimportant. The velocities for a number of gaseous explosives (chiefly hydrogen–oxygen or hydrocarbon–oxygen mixtures) were calculated by early investigators of the theory (43, 50) and found to be in good agreement with experimental velocities (8, 9, 21, 43, 50, 57). Their results are assembled in figure 1. Although these results were for many

years the sole verification of the hydrodynamic-thermodynamic theory, they are an altogether compelling verification of it.

The application of the hydrodynamic-thermodynamic theory to liquid and solid explosives does not provide a very stringent test of the theory, for it only shows that it is possible to predict detonation velocities if *reasonable* covolumes are assumed.

Recently the theory has been checked in three further ways: (*1*) Fox and Cairns have found the temperature T_1 spectroscopically, by assuming the radiation to be black-body and measuring its intensity at two or more wave lengths. (*2*) The velocity W_1 has been measured by x-ray photography (Clark) of charges containing alternate layers of explosive with and without lead ("zebra charges"). (*3*) The pressure P_1 can be computed from the initial velocity of the shock wave set up in a medium adjoining the explosive (e.g., lead, water, air).

The first of these methods measures only the heat/heat capacity ratio, not the covolume; the second and third methods measure only the covolume, not the heat or (appreciably) the heat capacity.[3]

Complete reports on these experiments are available elsewhere. The results of the experiments are found to be consistent with the hydrodynamic-thermodynamic theory.

D. PROPERTIES WITHIN THE REACTION ZONE

The pressure, temperature, and other properties appropriate to the partly decomposed explosive within the reaction zone can be found merely by inserting in equations 6 the value $N \cdot Q$ for the heat of reaction, where N is the fraction of the reaction completed.

For pressure, the result is:

$$P = \frac{D^2}{V_0} \cdot \frac{1 + \alpha/V_0}{1 + \gamma} \left\{ 1 + \sqrt{1 - \frac{N\Delta Q + \bar{C}_v T_0}{\Delta Q + \bar{C}_v T_0}} \right\} \tag{7a}$$

or since the first factor is merely P_1 and since ΔQ is much larger than $\bar{C}_v T_0$,

$$\frac{P}{P_1} \cong 1 + \sqrt{1 - N} \tag{7b}[9]$$

For temperature, the result is given by equation 8a below if the medium is supposed to be at constant temperature; even if the medium is heterogeneous, equation 8a gives the average temperature. If the partly decomposed explosive is (as we shall later offer evidence to indicate) composed in part of completely reacted material whose temperature rise is the sum of that due to chemical

[8] For

$$\frac{W_1}{D} = \frac{1 - \dfrac{\alpha}{V_0}}{1 + \alpha} \quad \text{and} \quad \frac{P_1 V_0}{D^2} = \frac{1 - \dfrac{\alpha}{V_0}}{1 + \alpha}$$

[9] Another possible solution would be equation 7b, but with a negative sign; this, however, is a spurious solution. See appendix D.

reaction and to compression, and in part of the unreacted residues of grains whose temperature rise is due only to compression, these two temperatures are given by equations 8b and 8c.

$$T_{\text{ave}} = (1 - N)T_0 + NT_1 + \frac{\gamma - 1}{2\gamma} T_1 \frac{P^2}{P_1^2} - NT_1 \frac{\gamma - 1}{2\gamma} \tag{8a}$$

$$T_{\text{ext}} = T_1 \left[1 + \frac{\gamma - 1}{2\gamma} \left(\frac{P^2}{P_1^2} - 1 \right) \right] \tag{8b}$$

$$T_{\text{int}} = T_0 + T_1 \frac{\gamma - 1}{2\gamma} \frac{P^2}{P_1^2} \tag{8c}$$

The weighted mean of the external temperature T_{ext} and the internal temperature T_{int} is equal to the average temperature T_{ave} (as of course it must be physically).

The result for material velocity W is

$$\frac{W}{W_1} = \frac{P}{P_1} \tag{9}$$

and the result for specific volume V is

$$\frac{1 - \dfrac{V}{V_0}}{1 - \dfrac{V_1}{V_0}} = \frac{P}{P_1} \tag{10}$$

The result for the ratio $(C + W)/D$ is

$$\frac{C + W}{D} = 1 - \left[1 - \frac{P}{P_1} \frac{1 + \dfrac{\alpha}{V_0}}{1 + \gamma} \right] \cdot \left[\sqrt{\frac{\gamma \dfrac{P}{P_1}}{\gamma + 1 - \dfrac{P}{P_1}}} - 1 \right] \tag{11}$$

Finally, the result for the entropy increase is

$$\Delta S = \Delta S_{V,T} + \bar{C}_V \ln \frac{T}{T_0} - R \ln \frac{V_0 - \alpha}{V - \alpha} \tag{12}$$

where $\Delta S_{V,T}$ is the entropy increase of the chemical reaction if it be assumed to take place at constant temperature and constant volume.[10] (If the explosive is supposed to be heterogeneous, the entropy rise must be computed by equation 10 for the exterior of the grains and the interior of the grains separately, and the two contributions added.)

All of the results given by equations 7 to 12 have been assembled and plotted in figure 2, which represents a detonation wave moving toward the reader's left. The computation has been made for TNT of density 1.57, but the results will be approximately the same for any other high explosive. Each property is plotted in figure 2 as a percentage of its final value.

[10] For details of the method of calculating $\Delta S_{V,T}$, see appendix E.

The properties immediately behind the front of the detonation zone, where the extent of reaction is still zero (subscript 0′), have a particular interest,
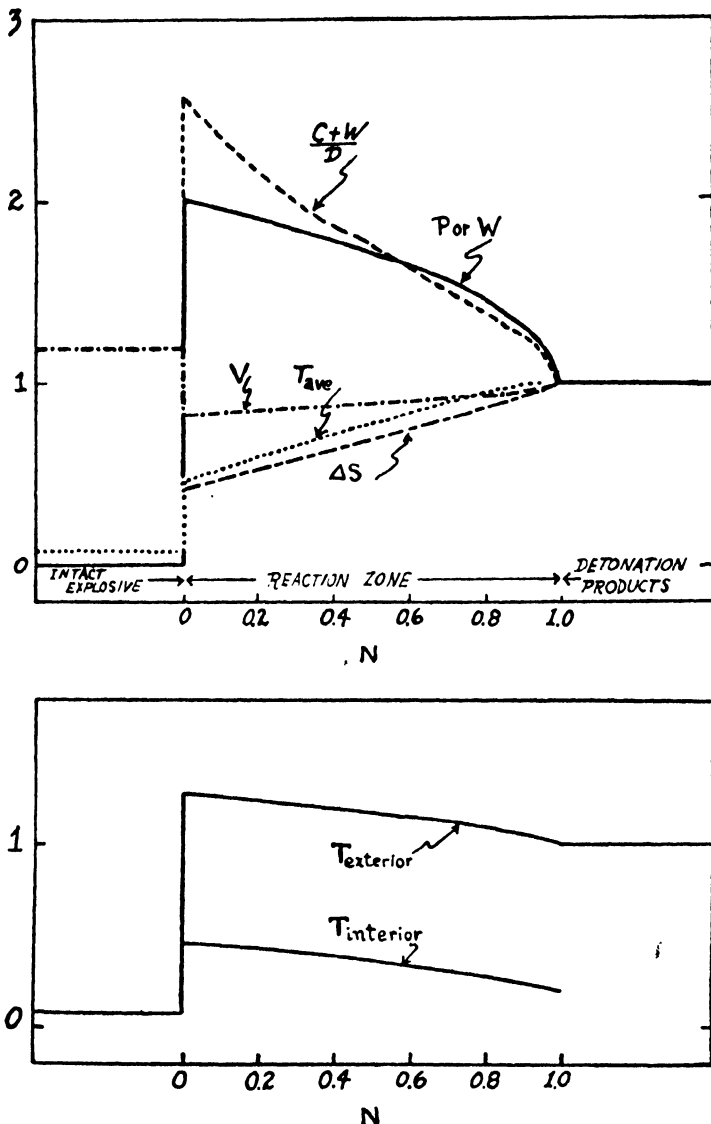
FIG. 2. Upper: Distribution of wave properties through the reaction zone. Lower: Temperature distribution for heterogeneous case.

since they are the properties behind a pure shock wave traveling with the velocity D in the intact explosive.

(a) The *pressure* at the shock front is precisely twice the pressure P_1, and is accordingly four times the pressure that would be found if the reaction oc-

curred at rest and at constant volume. This statement would of course be somewhat changed if a more elaborate equation of state for the unreacted material were employed. The *volume* and the *material velocity* show changes which would be expected from the corresponding pressure change.

(b) The *temperature* at the shock front is raised, but to a value considerably less than the final detonation temperature; the temperature here estimated is about 1500°C., but this estimate is closely bound up with the equation of state of the intact explosive and may be considerably in error. Moreover, in an explosive composed of grains the initial compression can hardly be uniform; a greater stress (and higher temperature) would exist near the points of contact and a smaller stress (and lower temperature) within the interior of grains. This conclusion is in accord with the evidence we shall present later, that the grains do not in fact become hot enough for reaction to proceed in their interior.

The temperature exterior to the grains is chiefly due to the heat of reaction, so it immediately reaches (or slightly exceeds) its final value T_1.

(c) The *entropy* shows a sharp increase at the shock front, followed by a gradual increase within the reaction zone as the reaction proceeds.

(d) The *ratio* $(C + W)/D$ is about 2.5 at the shock front, and does not reach unity until the end of the reaction zone. This means that in a pure shock wave the velocity of a rarefaction wave (which is $C + W$) is greater than the detonation velocity D, so that the rarefaction wave will continually eat away the shock wave; it is for this physical reason that no *steady* pure shock wave is possible. Further, those "microshocks" which are produced within the reaction zone by chemical reactions will at first travel with the local $C + W$, and therefore at a velocity higher than D; but they will attenuate as they travel, so they do not in the long run send any signal in advance of the detonation wave.

In the study of chemical decomposition which will take up much of the remainder of this paper, we shall then suppose the reaction to take place at temperatures and pressures in the reaction zone as given by figure 2.

The question arises: How is the reaction initiated? The reaction is surely initiated at the shock front, but theories differ as to the manner of the initiation there. The theory to which the authors subscribe is that the *temperature* is sufficient at the shock front—at least, in local regions as discussed above—to initiate chemical reaction in the ordinary way. This brings the initiation, as well as the subsequent reaction, into the province of ordinary chemical-kinetic theory. We know of no evidence inconsistent with this assumption.

Another theory (F. Eirich) holds that the *pressure* in a detonation wave is sufficient to bring about decomposition; the process is visualized as a sort of bending of one molecular grouping until it is in proximity to another grouping, whereupon the groups interact to yield decomposion products. Now in the first place Bridgman (14) has shown by direct experiment that high hydrostatic pressure has in itself no effect on explosives. In the second place, even if the entire differential detonation pressure could be applied across a single primary bond (which is highly unlikely), it would not present nearly enough force to break the bond and could at most stretch it a few hundredths of an Ångström or bend it a few tenths of an Ångström. In the third place, even granting that

one could by pressure move one grouping into proximity with another, still no reaction would occur unless it could occur spontaneously (i.e., exothermically) under those conditions; but practically every conceivable first step in the decomposition of organic nitro or nitroxy explosives, however juxtaposed or distorted the molecules be assumed, is *endothermic;* thus the theory is untenable from the point of view of detailed chemical mechanism. And in the fourth place, the decomposition rate predicted by this theory would be much too high (see below).

Yet another theory, proposed from time to time both in and out of print, is that the *material velocity* is responsible for initiation (for example, reference 72). This theory ascribes a special importance to the high translational velocity in the forward direction within the detonation wave. Impact of fast-moving molecules is visualized as tearing off fragments from intact molecules, thus initiating the reaction. The effect may properly be described as a "one-dimensional temperature," which would then amount to more than a thousand degrees. It is not easy to disprove the "one-dimensional temperature" hypothesis completely, but two arguments make a strong case against it. In the first place, let us assume that the kinetic energy of a fast molecule is delivered to a particular bond or grouping; then if dissociation takes place *before* the energy has time to become redistributed among the various vibrational degrees of freedom of the molecule, the dissociation can really be said to be caused by the impact; but if the dissociation does not take place until *after* the redistribution, the dissociation is merely due to the high temperature in the ordinary sense. We wish to know the rates of the competing processes,—dissociation and redistribution. Redistribution requires a small or 'zero activation energy, while dissociation requires a high activation energy (about equal to the strength of the bond broken); thus it is probable that redistribution will outrun dissociation, and the molecule will have reached a uniform temperature long before dissociation occurs.

The second argument against the material velocity theory is also an argument against the pressure theory of initiation, and appeals to the experimental observation (see Section II) that the reaction time is about 1 microsec. for typical explosives. According to either of the latter theories, the influence leading to initiation should affect all of the explosive material alike (since pressure and velocity are substantially homogeneous in the reaction zone); thus all the explosive in a cross-section would be simultaneously initiated. But any reasonable treatment of reaction rate indicates that then the reaction should be over in about one vibration period, or about h/kT seconds, which amounts to about 10^{-14} sec., or somewhat more than this when the effects of activation energy and activation entropy are included. The proponents of the latter theories are thus left with the problem of explaining, not why the decomposition in a detonation is so fast, but *why it is as slow as it is*—a discrepancy of about 8 powers of 10.

APPENDIX A: JUSTIFICATION FOR NEGLECT OF VISCOSITY AND THERMAL CONDUCTIVITY

Rigorously speaking, there is not at the shock front a discontinuity in pressure, temperature, velocity, and entropy. Rather, the transition takes place over a

narrow region whose length is determined by the viscosity and the thermal conductivity. If the length of this "shock zone" is very small in comparison with other lengths under consideration (e.g., the reaction zone length or the length of the rarefaction zone), the shock may without error be treated as a discontinuity. The length of the shock zone may be investigated for any particular case, by the inclusion of viscosity and thermal conductivity in the hydrodynamic equations.

For three-dimensional motion, the equations of motion[11] and of energy (74) are in vector notation:

$$\frac{d\overrightarrow{W}}{dt} = -V \operatorname{grad} P + \frac{1}{3}\eta V \operatorname{grad} \operatorname{div} \overrightarrow{W} + \eta V \nabla^2 \overrightarrow{W} \tag{A1}$$

$$\frac{dE}{dt} = \frac{dQ}{dt} - P\frac{dV}{dt} - 2\eta V \operatorname{div}(\overrightarrow{W} \operatorname{grad})\overrightarrow{W} - \frac{2}{3}\eta V(\operatorname{div}\overrightarrow{W})^2 + \kappa V \nabla^2 T \tag{A2}$$

where η is the viscosity and κ is the thermal conductivity. For one-dimensional motion these simplify to

$$\frac{dW}{dt} = -V\frac{\partial P}{\partial x} + \frac{4}{3}\eta V \frac{\partial^2 W}{\partial x^2} \tag{A3}$$

$$\frac{dE}{dt} = \frac{dQ}{dt} - P\frac{dV}{dt} + \frac{4}{3}\eta V \left(\frac{\partial W}{\partial x}\right)^2 + \kappa V \frac{\partial^2 T}{\partial x^2} \tag{A4}$$

and for a steady state, upon transformation to the coördinate system in which the shock wave is at rest:

$$P - P_0 + \frac{U^2}{V} - \frac{D^2}{V_0} = \frac{4}{3}\eta \frac{dU}{dy} \tag{A5}$$

$$\Delta E - \Delta Q - \frac{1}{2}(D - U)^2 - P_0(V_0 - V) = \frac{\kappa V_0}{D}\frac{dT}{dy} \tag{A6}$$

The pair of differential equations A5 and A6 has never been solved in closed form for general values of the parameters. For the case of a pure shock wave (ΔQ identically zero) R. Becker (6) expressed the temperature as a power series in the velocity, the series fortuitously terminating for the value $\kappa/\eta = C_p/3$. As an example of the calculation of shock zone length by Becker's method, we list the recent calculations by Thomas (69) for a shock wave in air. These calculations have taken into consideration the change of viscosity and conductivity with pressure and temperature.

Calculations for a shock wave in air

SHOCK PRESSURE	SHOCK ZONE LENGTH FREE PATHS
atm.	
4.5	3.98
9.8	3.08
19.7	2.25
43.4	1.98
	1.74

[11] The famous Navier-Stokes equation. See references 35, 49, 53, 58.

Similar calculations by Becker for a shock wave in liquid diethyl ether give the following results:

Calculations for a shock wave in ethyl ether

SHOCK PRESSURE	SHOCK ZONE LENGTH
atm.	*λ.*
100	520
1,000	53
10,000	6.5
100,000	1.4
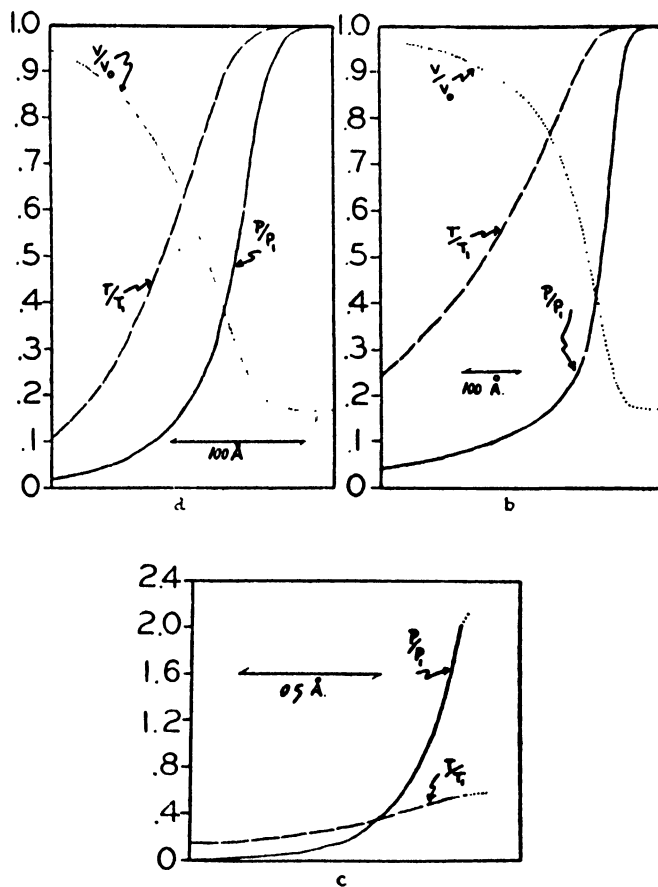
FIG. 3. Pressure, volume, and temperature distribution with η and κ

The structure of the shock zone is shown graphically in figures 3a, 3b, and 3c. Figure 3a is Becker's solution for a gas. Figure 3b is for a gas with a thermal conductivity four times as great as in Becker's solution (27). Figure 3c is for a solid explosive with an assumed viscosity of 0.2 centipoise and a thermal

conductivity of 10^4 ergs cm.$^{-2}$ sec.$^{-1}$ (28). The computation of figures 3b and 3c was carried through by a somewhat tedious step-by-step simultaneous numerical integration of the differential equations A5 and A6. Similar step-by-step computations have been carried through for a shock wave in which chemical reaction is occurring (27); not only are these calculations tedious and excessively sensitive to assumed boundary conditions, but for known explosives the reaction zone is so long in comparison with the shock zone (e.g., millimeters against Ångström units) that the shock zone may be analyzed on the assumption that no reaction has occurred.

The important qualitative result of all these computations is that the *shock zone is exceedingly narrow, amounting to a few free paths for a gas or a few molecules thickness for a solid*. One is thus justified in neglecting viscosity and conductivity when he is interested in the general structure of a detonation wave.

Rather than solve equations A5 and A6 rigorously, we may attack the problem by an alternative method which requires less mathematical labor and is more easily grasped intuitively.

First we consider viscous forces alone and set up a simplified model of the conditions behind and before the shock front. Suppose a number of molecules of very high average velocity to be brought adjacent to a number of molecules of very low average velocity. Then the initial velocity distribution at the interface is highly non-Maxwellian, and we wish to find the rate at which Maxwellian distribution is approached. Note that this is not a mere analogy, but a close description of what happens in a shock zone, where a portion of the directed energy (non-Maxwellian velocity distribution) is converted by viscous dissipation into temperature energy (Maxwellian velocity distribution) with an accompanying increase in entropy.

Now the problem of the "relaxation time of velocity distribution" has been solved in detail for gases (16, 44). Briefly, when a very fast-moving molecule collides with a slow-moving molecule, the fast molecule loses half its velocity. We see that any fluctuation in velocity will die out exponentially, roughly half of it disappearing in the time taken for each molecule to make one collision. We thus obtain a qualitative idea of the great rapidity of the process by which departures from Maxwellian velocity distribution are smoothed out. The corresponding problem for condensed phases has not been studied in detail, but here also there is little doubt that velocity differences will be smoothed out by a few collisions.[12] We may summarize by saying: So far as velocity (or pressure) is concerned, a shock zone thickness will be that within which a few molecular collisions have occurred.

Secondly, we consider the spread of temperature, and again set up a simplified model of the shock front. Suppose one stationary body at the shock temperature instantaneously to be brought adjacent to another stationary body at room temperature. Then we wish to find the rate at which temperature spreads from

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[12] In the theory of viscous flow, it has been assumed that the excess energy of a moving molecule is completely dissipated between one transport process of "jump" and the next (26). However, such a molecule undergoes some thousands of collisions between jumps.

the hot to the cold body, and to compare this with the rate at which the wave itself would travel.

This is a familiar problem in heat conduction, whose solution is

$$T/T_1 = 1 - 2Erf\left[x/\sqrt{2Vt/C_v}\right] \tag{A7}$$

and this solution is presented graphically in figure 4 for three different time intervals, along with the distance traveled by the shock wave in those same times. In this calculation the parameter $\kappa V/C_v$, which is roughly equal to velocity of sound $\times$ interatomic distance, was taken to be 0.018 cm.^{2} sec.$^{-1}$, a value appropriate for a solid explosive.

It will be observed that the spread of heat can keep pace with the travel of the shock wave for a distance of a few Ångström units, but not more. We may summarize: The temperature rise in a shock wave will run in advance of the pressure rise, but only for a distance amounting to a few interatomic distances.
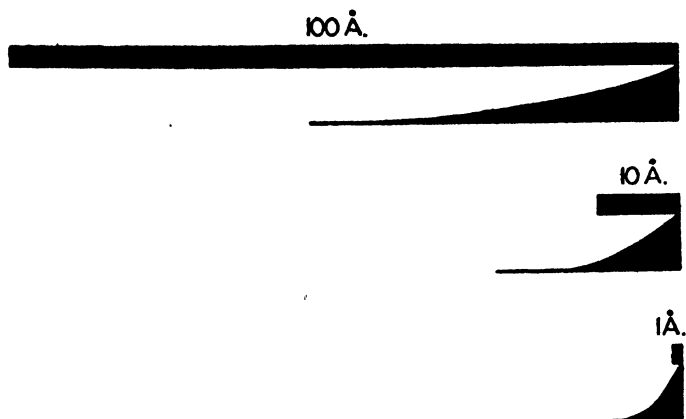
FIG. 4. Conduction range *vs.* velocity range

It is gratifying that both the rigorous numerical analysis and the simpler analysis lead to the same result, giving shock zones of molecular dimensions and thus justifying the neglect of viscosity and conductivity.

APPENDIX B: THE CHAPMAN–JOUGUET CONDITION

The equations of hydrodynamics do not suffice to determine the detonation velocity D uniquely. The additional assumption made by Chapman and by Jouguet, that the detonation is sonic with respect to the products at the end of the reaction zone,

$$D = W_1 + C_1 \tag{1e}$$

does permit an unique choice of the velocity. We proceed to examine the arguments offered to justify this Chapman–Jouguet condition.

To help visualize the problem, we plot equations 4b and 4c on a P,V diagram. Such a diagram, drawn approximately to scale for TNT, is figure 5. Equation

4b is a straight line

$$\frac{P - P_0}{V_0 - V} = \frac{D^2}{V_0^2} \qquad (4b)$$

whose slope is D^2/V_0^2. Equation 4c gives a graph which is hyperbolic in shape: thus for the Abel equation of state, equation 4c becomes, for small P_0:

$$P\left[V - V_0 \frac{2\alpha/V_0 + \gamma - 1}{2 + \gamma - 1}\right] = \frac{2R}{\gamma + 1}[T_0 + \Delta Q/\bar{C}_v]$$
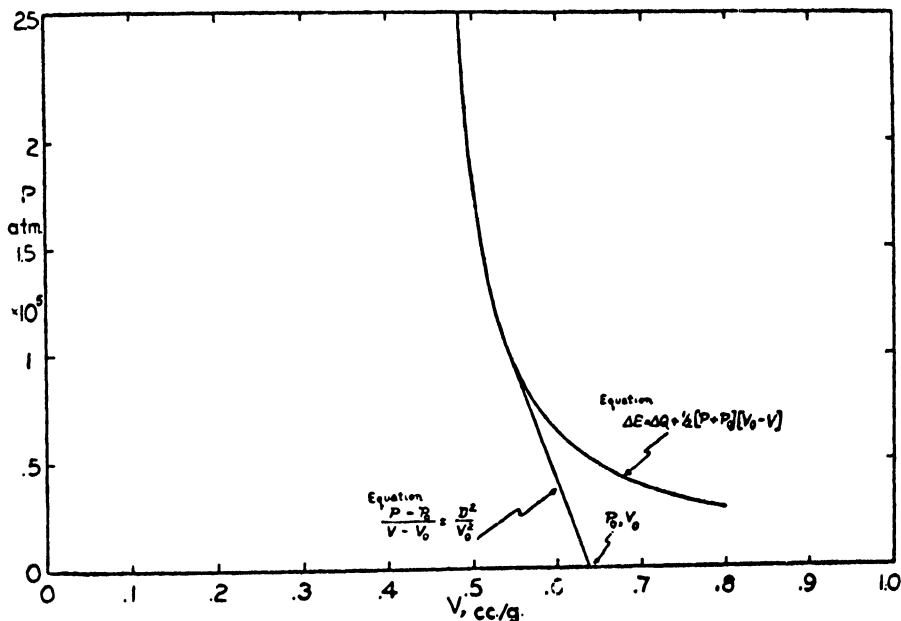
Fig. 5. Rankine–Hugoniot diagram for TNT of density 1.6 g./cc.

which resembles closely the Abel equation of state, but with special parameters replacing the covolume and the gas constant.

To determine the detonation velocity D, we wish to find the point of intersection of these two lines in the P,V diagram. The Chapman–Jouguet condition says that the desired intersection is the point of tangency of one line to the other, as the lines are drawn in figure 5. That this condition is identical with the condition $D = W_1 + C_1$ can be proved by algebraic manipulation of the equations of the two curves; or more elegantly by a geometrical method due to von Neumann. If we draw a straight line joining any two points of the hyperbola representing complete reaction, that straight line will represent a shock wave in the completely reacted material. If we let the two points approach one another, the straight line becomes tangent to the curve and represents a sonic wave in the reacted material.

Inspection of figure 5 shows that the Chapman–Jouguet condition can be

stated in several other ways which are geometrically equivalent. Thus (*i*) the Chapman–Jouguet velocity is the only detonation velocity which is uniquely specified; also (*ii*) the Chapman–Jouguet velocity is the minimum detonation velocity compatible with the hydrodynamic equations. (It was in this latter form that Chapman assumed the condition.)

Discussion according to von Neumann

von Neumann (73) has pointed out that if the reaction zone in a detonation wave is finite, the hydrodynamic and thermodynamic equations must be valid at all points within the wave, so that one can draw a family of Hugoniot curves corresponding to successive amounts of chemical reaction, from $N = 0$ to $N = 1$. Now the straight line which represents conditions within the shock wave must begin somewhere on the curve $N = 0$, must intersect the curves for increasing N in order, and must end somewhere on the curve $N = 1$. In order that there
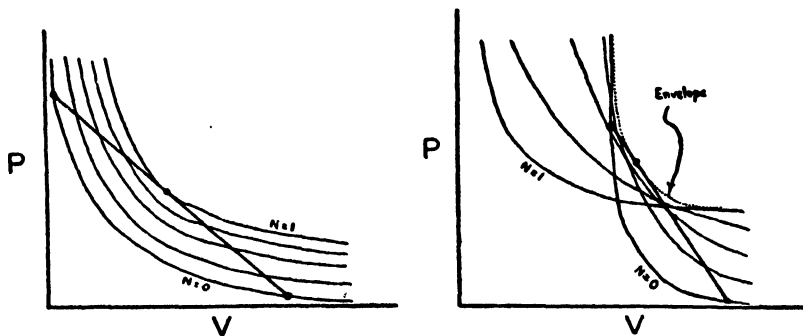
FIG. 6. von Neumann's curves

exist a discontinuity in pressure and temperature at the shock front so as to initiate the reaction, the intersection of the straight line with the curve $N = 0$ must be the *upper* intersection. If the straight line intersects the curve $N = 1$ at an upper intersection point, the tangent to the curve at that point would be steeper, so the velocity of sound in the products would exceed the detonation velocity and a rarefaction wave would engulf the detonation wave; thus the intersection with the curve $N = 1$ must be the *lower* intersection.

In order to proceed continuously from an upper intersection at $N = 0$ to a lower intersection at $N = 1$, either (*i*) the upper intersection and the lower intersection coincide at $N = 1$, giving a point of *tangency* (this is the usual Chapman–Jouguet result), or (*ii*) if the curves cross one another so that an envelope exists, the straight line may be tangent to the envelope. These two possibilities are given graphically in figure 6, taken from von Neumann's paper. The latter possibility, which was first proposed in the paper by von Neumann, does not correspond to any known physical situation.

Discussion according to Scorah

Scorah (65) has shown by straightforward thermodynamics that at the Chapman–Jouguet velocity the entropy increase is a minimum; also that the ratio

entropy increase/available energy fed into the wave front is a maximum. Scorah states: "The normal detonation wave proceeds at that speed which allows the greatest degradation of each unit of energy supplied to the wave. This result is in accord with the fundamental principle of degradation of energy in all natural processes—a principle that is so universally verified that when the extent of degradation brought about by a natural process is discovered to vary with the speed of the process, it would seem only consistent that the stable speed would be that which allowed the greatest degradation." Since this principle is not derivable from the second law of thermodynamics, nor is it generally valid for chemical kinetics, the argument must be regarded as one of plausibility rather than of strict proof. The result is nevertheless an interesting one.

Discussion according to Devonshire

Jouguet originally justified his assumption by appealing to considerations of stability of the wave. Devonshire (20) and also Eyring et al. (29) have extended the method to include waves other than ideal steady waves, thus obtaining a generalized Chapman–Jouguet condition.

The derivation has been carried through for three cases: (i) the wave is non-planar; (ii) the wave is not in its steady state; (iii) the wave is both non-planar and non-steady.

Case (i): Non-planar wave

Suppose the propagating wave to be symmetric about an axis (plane), and represent the wave front in a small region by a spherically (cylindrically) curved surface. Denote the radius of curvature of the wave front by r_0, and the angle between the radius vector and the axis (plane) of symmetry by ϕ. If the components of particle velocity in a fixed coördinate system are W_r in the radial direction and W_ϕ in the direction of increasing ϕ, in a coördinate system moving with velocity D these are

$$U_r = W_r - D \cos \phi \tag{B2}$$

$$U_\phi = W_\phi + D \sin \phi \tag{B3}$$

A steady state is assumed, so that at the axis (plane) of symmetry

$$\frac{d}{dt} = -(D - W_r)\frac{d}{dr}$$

whereupon the equations of continuity and of motion become, near the wave front

$$(D - W_r)\frac{dV}{dr} = -V\frac{dW_r}{dr} - \frac{kV}{r}\left[W_r + \left(\frac{\partial W_\phi}{\partial \phi}\right)_{\phi=0}\right] \tag{B4}$$

$$(D - W_r)\frac{dW_r}{dr} = V\frac{dP}{dr} \tag{B5}$$

where k is 2 for spherical waves and 1 for cylindrical waves.

By the equation of state, the pressure is a function of the three variables T,

V, and N. But the first law of thermodynamics gives us another relation between T, V, and N, so that any one of these variables may be eliminated from the equation for pressure. (It is not necessary to write explicitly the first law relation between T, V, and N; the mere fact that such a relation exists is sufficient.) Then

$$P = P(V, N)$$

$$\frac{dP}{dr} = \left(\frac{\partial P}{\partial V}\right)_N \frac{dV}{dr} + \left(\frac{\partial P}{\partial N}\right)_V \frac{dN}{dr} \tag{B6}$$

Of these derivatives, one is determined by the velocity of sound C:

$$\left(\frac{\partial P}{\partial V}\right)_N = \left(\frac{\partial P}{\partial V}\right)_{N,S} = -\frac{C^2}{V^2} \tag{B7}$$

We define a new quantity χ such that

$$\chi = \left(\frac{\partial P}{\partial N}\right)_v \frac{dN}{dt} = -(D - W_r)\left(\frac{\partial P}{\partial N}\right)_v \frac{dN}{dr} \tag{B8}$$

so that with the two substitutions B7 and B8, equation B6 becomes

$$\frac{dP}{dr} = -\frac{C^2}{V^2}\frac{dV}{dr} - \frac{\chi}{D - W_r} \tag{B9}$$

With this substitution into the equations of continuity and of motion, we obtain:

$$-\frac{(D - W_r)}{V}[(D - W_r)^2 - C^2]\frac{dV}{dr}$$

$$= (D - W_r)^2 \frac{k}{r}\left[W_r + \left(\frac{\partial W_\phi}{\partial \phi}\right)_{\phi=0}\right] - \chi V \tag{B10}$$

$$[(D - W_r)^2 - C^2]\frac{dW_r}{dr} = \frac{C^2 k}{r}\left[W_r + \left(\frac{\partial W_\phi}{\partial \phi}\right)_{\phi=0}\right] - \chi V \tag{B11}$$

As one proceeds through the wave three possibilities may occur:

(I) $D < W_r + C$ throughout. Any rarefaction wave arising in the products will travel at a sonic velocity with respect to the products, or $W_r + C$. Such a wave would move faster than the detonation, and hence engulf and destroy it.

(II) $D = W_r + C$ at a point where the right sides of equations B10 and B11 are (positive or negative) finite. In this situation the derivatives dV/dr and dW_r/dr become (positively or negatively) infinite, so that a shock discontinuity is occurring within the detonation wave. It may be assumed that any such discontinuity would be only a transient, would rapidly propagate to the front or rear of the detonation wave, and would there be destroyed.

(III) $D = W_r + C$ at a point where the right sides of equations B10 and B11 vanish; thus where

$$\chi = \frac{kC^2}{Vr}\left[W_r + \left(\frac{\partial W_\phi}{\partial \phi}\right)_{\phi=0}\right] \tag{B12}$$

This is the desired solution for the generalized Chapman–Jouguet condition for a non-planar wave.

Note that for the special case treated by von Neumann, that with no radial loss, this becomes $\chi = 0$, therefore

$$\left(\frac{\partial P}{\partial N}\right)_v \frac{dN}{dr} = 0$$

The vanishing of dN/dt means that the Chapman–Jouguet point is at the end of the chemical reaction; or the vanishing of $\left(\frac{\partial P}{\partial N}\right)_v$ is the condition for the Chapman–Jouguet point to lie on the envelope of Hugoniot curves. The present result thus includes von Neumann's result.

In order to assess this result, we examine again the continuity equation B4 with the substitution B9:

$$\frac{dP}{dr} = \frac{C^2/V}{D - W_r} \frac{dW_r}{dr} - \frac{kC^2/V}{(D - W_r)r} \left[W_r + \left(\frac{\partial W_\phi}{\partial \phi}\right)_{\phi=0} \right] - \frac{\chi}{D - W_r} \quad \text{(B13)}$$

Clearly the first term on the right is the rate of pressure change due to the change in particle velocity, which would be found even in passing through an ideal wave. The second term is the rate of pressure change due to curvature of the wave front and the interaction between adjacent elements of fluid. The third term is the rate of pressure change due to chemical reaction. When the condition B12 holds, the last two terms drop out. We may now summarize by saying: The detonation velocity for a wave with a curved front is given by $D = C_{cJ} + W_{cJ}$, where C_{cJ} and W_{cJ} are evaluated at that point where the rate of pressure rise due to reaction is just equal to the rate of pressure fall due to the curvature of the front and the interaction of neighboring elements of the fluid. For a convex wave of high curvature, the effective reaction zone will be shortened.

Case (ii): Time-dependent planar wave

If a plane wave is propagating with the instantaneous (but not steady) velocity D, we write the equations of continuity and motion in a coördinate system moving with this velocity so that $y = Dt - x$:

$$(D - W) \frac{\partial V}{\partial y} = -V \frac{\partial W}{\partial y} + \frac{\partial V}{\partial t} \quad \text{(B14)}$$

$$(D - W) \frac{\partial W}{\partial y} = V \frac{\partial P}{\partial y} - \frac{\partial W}{\partial t} \quad \text{(B15)}$$

As before, the equation of state furnishes the relation

$$\frac{\partial P}{\partial y} = \left(\frac{\partial P}{\partial V}\right)_{N,S} \frac{\partial V}{\partial y} + \left(\frac{\partial P}{\partial N}\right)_{V,S} \frac{\partial N}{\partial y} + \left(\frac{\partial P}{\partial S}\right)_{V,N} \frac{\partial S}{\partial y} \quad \text{(B16)}$$

or

$$\frac{\partial P}{\partial y} = -\frac{C^2}{V^2} \frac{\partial V}{\partial y} + \frac{\chi}{D - W} \quad \text{(B17)}$$

where C is the velocity of sound and χ is defined as

$$\chi = (D - W)\left\{\left(\frac{\partial P}{\partial N}\right)_{V,S}\frac{\partial N}{\partial y} - \left(\frac{\partial P}{\partial S}\right)_{N,V}\frac{\partial S}{\partial y}\right\}$$

$$= \left(\frac{\partial P}{\partial N}\right)_{V,S}\left(\frac{dN}{dt} - \frac{\partial N}{\partial t}\right) + \left(\frac{\partial P}{\partial S}\right)_{V,N}\left(\frac{dS}{dt} - \frac{\partial S}{\partial t}\right) \tag{B18}$$

As before, the substitution of B17 into the equation of continuity and motion gives two new equations

$$-\frac{D - W}{V}[(D - W)^2 - C^2]\frac{\partial V}{\partial y} = V\chi - (D - W)\frac{\partial W}{\partial t} + \frac{(D - W)^2}{V}\frac{\partial V}{\partial t} \tag{B19}$$

$$[(D - W)^2 - C^2]\frac{\partial W}{\partial y} = V\chi - (D - W)\frac{\partial W}{\partial t} + \frac{C^2}{V}\frac{\partial V}{\partial t} \tag{B20}$$

and again there are three possibilities, of which two are ruled out by instability. Then the instantaneous detonation velocity will be given by $D = C + W$ at the point where

$$\chi = \frac{C}{V}\frac{\partial W}{\partial t} - \frac{C^2}{V^2}\frac{\partial V}{\partial t} \tag{B21}$$

To interpret this result, we write

$$\frac{\partial P}{\partial y} = \frac{C^2/V}{(D - W)^2}\frac{\partial W}{\partial t} - \frac{1}{D - W}\left\{\frac{C^2/V}{D - W}\frac{\partial W}{\partial t} - \frac{C^2}{V}\frac{\partial V}{\partial t}\right\} + \frac{\chi}{D - W} \tag{B22}$$

in which it is evident that the second term on the right gives the space rate of decrease of pressure due to the time rate of change of velocity and volume, while the third term is the space rate of increase of pressure due to the space rate of change of chemical composition and entropy. These two rates are equal at the Chapman–Jouguet point, where $D = W + C$.

For a rapidly accelerating wave, the effective reaction zone will be shortened.

Case (iii): Time-dependent non-planar wave

Finally, if a detonation wave is propagating both with a curved front and at a velocity different from its equilibrium velocity, we write the equations of continuity and motion near the wave front as:

$$\frac{dV}{dt} = V\frac{\partial W}{\partial r} + \frac{kW}{Vr} \tag{B23}$$

$$\frac{dW}{dt} = -V\frac{\partial P}{\partial r} \tag{B24}$$

Proceeding with the analysis as before, we find that $D = W + C$ at the point where

$$\chi = \frac{D - W}{V}\frac{\partial W}{\partial t} - \frac{C^2}{V^2}\frac{\partial V}{\partial t} + \frac{kC^2 W}{Vr} \tag{B25}$$

We may now state a generalized version of the Chapman–Jouguet condition for a wave both non-planar and non-steady:

The detonation velocity is given by $D = C_{cj} + W_{cj}$, where C_{cj} and W_{cj} are evaluated at that point where the space rate of increase of pressure due to the space rate of change of chemical composition and entropy is just equal to the sum of the space rate of decrease of pressure due to the time rate of change of velocity and volume and that due to the curvature of the wave-front.

(B26)

For any detonation wave whose deviation from planarity and from its equilibrium velocity is not large, the Chapman–Jouguet point will be very near to the point where the chemical reaction becomes complete. We shall always assume this to hold in subsequent sections of the present study, with the exception of the investigation of highly curved waves where the effect of curvature will be explicitly included.

APPENDIX C: EXACT DETONATION PROPERTIES

The exact equations for a detonation wave in which the initial pressure P_0 is too large to be neglected are the following:

$$\frac{V_1}{V_0} = \frac{\gamma + \dfrac{\alpha}{V_0} - \dfrac{\alpha}{V_0} \cdot \dfrac{P_0}{P_1}}{\gamma + 1 - \dfrac{P_0}{P_1}}$$

$$P_1 = \frac{2R}{V_0 - \alpha} \frac{\Delta Q + \bar{C}_v T_0}{\bar{C}_v} \frac{1 + \dfrac{\gamma - 1}{\gamma + 1} \cdot \dfrac{P_0}{P_1}}{1 + \dfrac{1}{\gamma + 1} \cdot \dfrac{P_0}{P_1}}$$

$$T_1 = \frac{\Delta Q + \bar{C}_v T_0}{\bar{C}_v} \cdot \frac{2\gamma}{\gamma + 1 - \dfrac{P_0}{P_1}}$$

$$D^2 = (\Delta Q + \bar{C}_v T_0) \frac{2(\gamma^2 - 1)}{\left(1 - \dfrac{\alpha}{V_0}\right)^2} \frac{1 + \dfrac{\gamma - 1}{\gamma + 1} \dfrac{P_0}{P_1}}{1 - \dfrac{P_0}{P_1}}$$

$$\frac{W_1}{D} = \frac{\left(1 - \dfrac{\alpha}{V_0}\right)\left(1 - \dfrac{P_0}{P_1}\right)}{1 + \gamma - \dfrac{P_0}{P_1}}$$

APPENDIX D: SPURIOUS SOLUTION FOR THE PROPERTIES WITHIN THE REACTION ZONE

If the negative sign is taken in equation 7b, the properties within the reaction zone would be those plotted in figure 7. It will be noticed that at the wave front

there is no change in pressure, temperature, particle velocity, or entropy. From a chemical point of view, there is nothing at such a front to initiate reaction. This solution therefore represents no known physical situation, and must be treated as spurious.
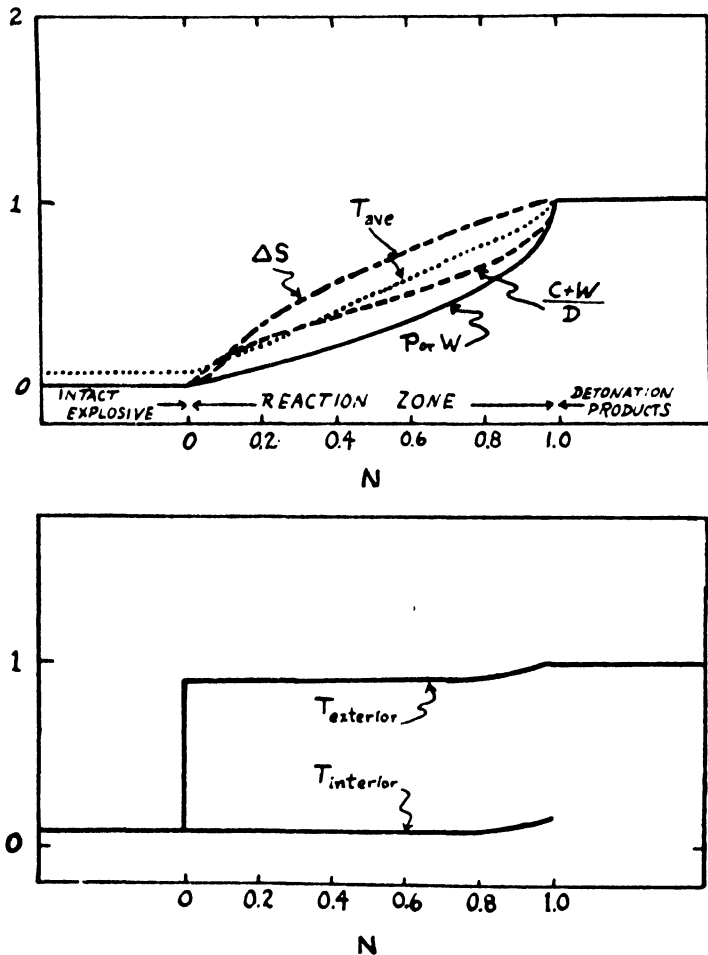
Fig. 7. Upper: Distribution of wave properties through the reaction zone; spurious solution. Lower: Temperature distribution for the heterogeneous case; spurious solution.

APPENDIX E: ENTROPY CHANGE OF EXPLOSION AT CONSTANT VOLUME AND TEMPERATURE

The entropy increase across a shock front can be calculated at once from the temperature and the volume before and behind the wave front when the equation of state is known. In a detonation wave there is an additional contribution to the entropy increase, because the detonation products are chemically different from the intact explosive. We calculate this entropy change of chemical decom-

position at constant temperature and volume, by carrying out the change in two hypothetical steps.

Step 1: The explosive at room temperature decomposes to form its products of detonation also at room temperature, but at the volume they would occupy each at a partial pressure of 1 atm. This is the usual standard state for entropies which are tabulated for the products and can be estimated rather closely for the intact explosives.

Step 2: The products, at the volume they would occupy each at a partial pressure of 1 atm., are compressed to a volume equal to the original volume. The products will be supposed to obey the Abel equation of state.

The entropy change is for this sequence of processes

$$\Delta S = S^0_{products} - S^0_{explosive} - R \ln \frac{V_{atm} + \alpha}{V_0 - \alpha} \tag{E1}$$

The calculation may be clarified by two examples:

Example 1: TNT of density 1.6. Reaction assumed to be:

$$\rightarrow \quad \tfrac{3}{2}N_2 \quad + \quad \tfrac{5}{2}H_2O \quad + \quad CO \quad + \quad 6C$$
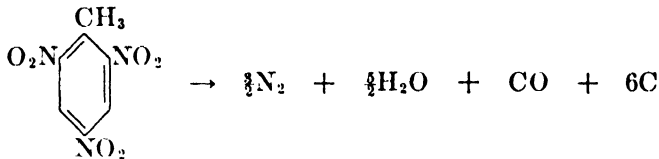
Step 1: S^0 of 3/2 mole gaseous N_2 .... 1.5×45.79

S^0 of 5/2 mole gaseous H_2O .... 2.5×45.13

S^0 of 1 mole gaseous CO 47.32

S^0 of 6 moles solid C .... 6×1.36

$-S^0$ of 1 mole solid TNT .... -65

___

Entropy change per mole TNT .... 172 E.U.

Entropy change per gram TNT .... 172/239 = 0.720 E.U.

Step 2: $R = \dfrac{1.986}{\text{Mean mol. wt. gaseous products}} = \dfrac{1.986}{23} = 0.0864$ cal. deg.$^{-1}$ g.$^{-1}$

$V_0 = 0.636$ cm.^{3} g.$^{-1}$

$\alpha = 0.4225$ cm.^{3} g.$^{-1}$ assumed

$V_{atm} = \dfrac{24,500 \times (3/2 + 5/2 + 1)}{239} = 512$ cm.^{3} g.$^{-1}$

Entropy change per gram $= -0.0864 \ln \dfrac{512}{0.2135} = -0.680$

$$\Delta S_{T,V} = +0.040$$

Example 2: PETN of density 1.6. Reaction assumed to be:

$$O_2NOCH_2\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{\overset{|}{\underset{|}{C}}}}CH_2ONO_2 \rightarrow 2N_2 + 4H_2O + 3CO_2 + 2CO$$
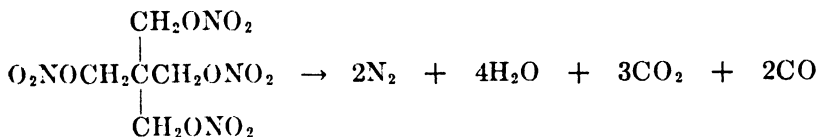
Step 1: S^0 of 2 moles gaseous N_2 .... 2×45.79

S^0 of 4 moles gaseous H_2O . ... 4×45.13

S^0 of 3 moles gaseous CO_2 .... 3×51.07

S^0 of 2 moles gaseous CO .... 2×47.32

$-S^0$ of 1 mole solid PETN .... -2×55

Entropy change per mole PETN .... 465 E.U.

Entropy change per gram PETN .... $465/316 = 1.47$ E.U.

Step 2: $R = \dfrac{1.986}{28.7} = 0.0691$ cal. deg.$^{-1}$ g.$^{-1}$

$V_0 = 0.625$ cm.^{3} g.$^{-1}$

$\alpha = 0.41$ cm.^{3} g.$^{-1}$ assumed

$V_{atm} = \dfrac{24,500 \times (2 + 4 + 3 + 2)}{316} = 852$ cm^3. g.$^{-1}$

Entropy change per gram $= -0.0691 \ln \dfrac{852}{0.215} = -0.573$

$$\Delta S_{T,V} = +0.897$$

II. THE NON-IDEAL DETONATION WAVE

A. INTRODUCTION

Even the earliest investigators of detonation (*viz.*, Berthelot and Vieille) noticed that if the detonation were sent through a tube of too small a diameter, it traveled with less than its full velocity. With the more recent extension of detonation velocity measurements over a wide variety of liquid and solid explosives, it has become a commonplace observation that the detonation velocity in a narrow stick is below its ideal value. Thus in any program of measurement of a detonation velocity, one is careful to repeat the measurement using explosive charges of greater and greater diameter until he is sure he has eliminated the effect of charge diameter on the detonation velocity.

Although this phenomenon has been known for many years, a good theory of its cause was not until recently to be found in the literature.[13] One formulation of the now generally accepted explanation was put forward by Jones (40) in

[13] Thus, as recently as 1938, Parisot and Laffitte (56) ascribed the effect to chain breaking by the walls. While this would produce a longer reaction zone, that does not of itself lead to a lower detonation velocity, since the hydrodynamic-thermodynamic ideal velocity does not depend on reaction zone length.

1942. If the reaction occurs over a finite zone, the high pressure within that zone will have led to an appreciable lateral expansion before the reaction becomes complete; the consequent drop in pressure and temperature will lead to a decrease in detonation velocity. Otherwise stated, not all of the energy of the explosive is available to maintain the full detonation velocity, because a portion of the energy is dissipated out the sides of the explosive charge. The theory may be briefly described as the *lateral-loss theory*. It can be seen intuitively—and will also be shown by detailed mathematical analysis—that the effect of lateral loss on the detonation velocity becomes significant when the radius of the explosives charge is of the same order of magnitude as the reaction zone length. Another phenomenon which was observed first for gaseous explosives and later for solid explosives is that an explosive charge initiated at a velocity below its ideal velocity (as by a weak priming charge) does not immediately attain its ideal velocity. Rather, the velocity builds up gradually and approaches its ideal value asymptotically.

A theory of the building-up rate as a function of the reaction zone length has been developed by the authors (29), who find that the detonation velocity covers half the difference between its initial value and its ideal value in a distance of a few reaction zone lengths. The details of the theory will be given below.

Finally, the detonation wave may experience such severe losses that the wave can no longer propagate stably, so that failure of the detonation occurs. This failure phenomenon has been found in experimental detonation velocity measurements—the trace of the detonation on the photographic plate ends abruptly, and the undamaged remainder of the charge can be recovered later. The same phenomenon, also called "fading," has been encountered in the service use of high explosives.

One theory of the failure process says first, that any lateral losses will lead both to a lower detonation velocity and a lower temperature; the lower temperature will lead to a slower reaction and a longer reaction zone; this in its turn will lead to additional losses. When the cumulative effect becomes sufficiently great, failure will occur. The details of the theory will be given below.

It will be noticed that in the theories of all three non-ideal waves—the wave in a finite charge, the transient building-up wave, the failing wave—the reaction zone length plays a leading role. If one understands the chemical reaction kinetics in a detonation explosive well enough, he can predict the reaction zone length under any desired conditions, and so the stability of the propagating wave. In this way, it should be possible to develop a rational approach to such technical problems as, say, boostering of explosive charges. However, not enough facts are now known concerning the chemical kinetics of detonation to make such a program feasible.

Another approach, and a more fruitful one from the point of view of fundamental investigation, will be followed here. That is *to use the theories in an inverted sense, in order to determine by measurements on non-ideal waves the reaction zone lengths in detonating explosives*. By suitable variation of the external conditions, it is possible to study in this way the kinetics of the chemical reaction in a

detonation—even though such a chemical reaction is complete in less than one millionth of a second!

B. THE FINITE CHARGE

1. *Introduction*

Two theoretical treatments of the non-ideal detonation velocity in a cylindrical stick of explosive of finite radius have appeared. One treatment is by H. Jones (40) and the other is by the present authors (29). The two theories have in common their basic assumption: Of the hydrodynamic equations, only the equation of continuity is perturbed by the expansion in the reaction zone. The two theories, after all the mathematical details have been worked out, also yield numerically similar results.
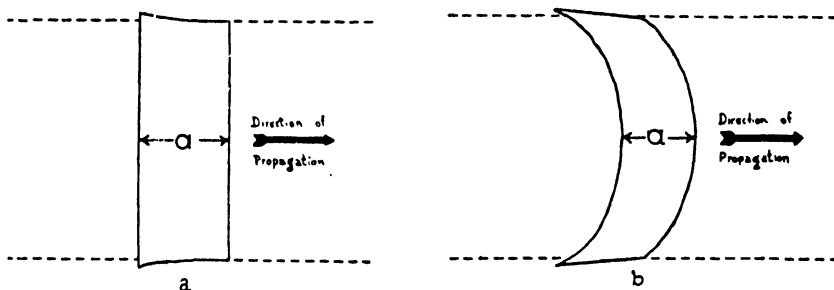
Fig. 8. Models for nozzle theory and curved-front theory. (a) Reaction zone in a detonation, as visualized in the theoretical treatment by H Jones. (b) Reaction zone in a detonation, as visualized in the theoretical treatment by H. Eyring and coworkers. The two figures are drawn approximately to the correct proportions for a detonation wave in a stick of solid explosive propagating at a velocity 75 per cent of the total velocity, as calculated according to the respective theories.

But the methods of working out the two theories are quite different. Figure 8 represents (approximately to scale) the reaction zone in a detonation, as visualized in the respective theories.

Jones pictures the reaction as beginning at a plane shock front, and becoming complete at another plane the reaction zone length a distant. As seen by an observer moving with the detonation velocity, the detonating stick of explosive looks like a material issuing from a nozzle, the mouth of the nozzle being situated at the wave front. The first step in Jones's theory is to solve the hydrodynamic equations to find the relationship between the expansion of the stream tube and the velocity of propagation. The second step in Jones's theory is to find the amount of expansion for various types of confinement, thus: (*i*) for unconfined or lightly confined charges, the outer layers of explosive are assumed to follow the flow lines given by Meyer's solution for flow around a corner, while the inner part of the explosive expands at constant pressure in a cross-section; (*ii*) for moderately heavily cased charges, the expansion is determined by the motion of the case, which is being accelerated outward because of the pressure in the explosive; and (*iii*) for extremely heavily cased charges, the expansion of the case

is brought about by a shock wave sent into the case. The theory developed by Jones will hereinafter be referred to as the "nozzle" theory.

Alternatively, one may suppose that the reaction zone is curved into a lens-shaped figure convex at the front, the argument running as follows: At the edge of the charge a rarefaction wave will be sent into the reaction zone. Since the local velocity of sound is greater than the detonation velocity, such a rarefaction wave will overtake the front of the wave and slow down the edge of the wave front, thereby giving rise to a curved front. This process will continue until the angle of intersection of the wave front with the edge of the charge is small enough so that the rarefaction wave is no longer reflected. The steady-state velocity will now be below that of a plane wave because of the curvature of the front.

Accordingly, the first step in this theory is to solve the hydrodynamic equations to find the relationship between curvature of the wave front and the velocity of propagation. The second step is then to find, by a graphical construction, the actual shape of the wave for any desired degree of confinement, thus: (i) for unconfined charges, the angle of intersection of the edge of the shock wave with the case is 90°; (ii) for moderately cased charges, the angle is determined by the expansion of the case; and (iii) for heavily cased charges, the angle is determined by the velocity of the shock wave sent into the case. This theory will hereinafter be referred to as the "curved-front" theory.

We now proceed to the mathematical details of the two theories.

2. Nozzle theory

(a) The effect of expansion[14]

If the streamlines within the reaction zone are nearly parallel to the charge axis (as they would be for small expansions), the approximate equation of continuity is

$$\frac{V}{V_0} = \frac{U}{D} r^2 \tag{1}$$

where r is the relative expansion of the stream tube. For small expansions, no considerable amount of momentum or energy is lost by lateral motion, and the Chapman-Jouguet condition is also identical with that for a plane wave. Thus we may at once write down the three equations (motion, energy, and Chapman-Jouguet) which are, for an intense wave in a perfect gas:

$$P + \frac{U^2}{V} = \frac{D^2}{V_0} \tag{2}$$

$$\frac{\gamma}{\gamma - 1} PV + \tfrac{1}{2} U^2 - \tfrac{1}{2} D^2 = \Delta Q + \bar{C}_v T_0 \tag{3}$$

$$U_1^2 = P_1 V_1 \gamma \tag{4}$$

[14] For the sake of uniformity we have here changed Jones's notation into that used throughout this paper. We have also slightly simplified Jones's original derivation at a few minor points.

We also recall that the detonation velocity D_i of an ideal plane wave in the gaseous explosive here described is (see Section I):

$$D^2 = 2(\Delta Q + \bar{C}_v T_0)(\gamma^2 - 1) \tag{5}$$

Upon combining these five equations, we obtain without difficulty the final equation

$$\frac{D_i^2}{D^2} = 1 + \gamma^2(r_1^4 - 1) \tag{6}$$

or numerically

$$\frac{D_i^2}{D^2} \cong 1 + 2.25(r_1^4 - 1)$$
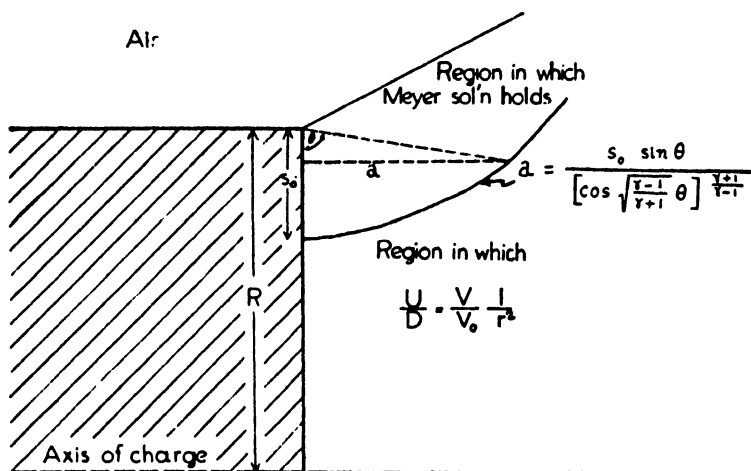
Fig. 9. Jones's construction for nozzle theory

This equation relating the detonation velocity to the relative expansion of a central stream tube at the end of the reaction zone is the foundation upon which all the further nozzle theory of finite charges is built.

(b) The uncased charge

Instead of actually finding the expansion at the end of the reaction zone length a of reacting explosive, which would be very difficult, Jones finds the corresponding radial expansion in the same distance of reaction product gases assumed to be expanding adiabatically. The one process should bear a satisfactorily close resemblance to the other.

Figure 9 represents gas issuing from a nozzle at a velocity equal to the local velocity of sound, it being desired to find the expansion at a distance a from the nozzle. This itself is a problem in hydrodynamics which had not been previously solved, but for which Jones succeeded in obtaining a good approximate solution.

The flow from the nozzle is considered to be separable into two regions. In

the outer region, the stream lines will be those of Meyer's solution for the flow around an edge, the equation for which is:

$$a = s_0 \frac{\sin \theta}{\left[\cos \sqrt{\dfrac{\gamma - 1}{\gamma + 1}} \theta \right]^{(\gamma+1)/(\gamma-1)}} \tag{7a}$$

where the gaseous products are assumed to obey the polytropic equation

$$PV^\gamma = \text{const.} \tag{8}$$

With the exponent $\gamma = 3$, the Meyer streamlines are

$$a = s_0 \frac{\sin \theta}{\cos^2 \dfrac{\theta}{\sqrt{2}}} = s_0 \frac{2 \sin \theta}{1 + \cos \sqrt{2\theta}} \tag{7b}$$

The relative expansion along any Meyer streamline is easily found, for from the evident geometry of the system

$$r = \frac{R - a \operatorname{ctn} \theta}{R - s_0} = \frac{R}{R - s_0} \left[1 - \frac{a}{R} \operatorname{ctn} \theta \right] \tag{9a}$$

In the inner region the streamlines are assumed to be sufficiently nearly parallel to the axis, so that the equation of continuity is

$$\frac{U}{D} = \frac{V}{V_0} \frac{1}{r^2} \tag{10}$$

the relative expansion and the pressure remaining constant across this internal stream tube. It is the relative expansion in this region we desire to find. Since the relative expansion can readily be found along any Meyer streamline from equations 7b and 9, it only remains to choose a value of s_0 such that the Meyer streamline is most nearly representative of the interior streamlines.

The choice of the best Meyer streamline is made in the following manner: The pressure along a Meyer streamline is calculated according to the equation

$$\frac{P_{\text{Meyer}}}{P_1} \left(\cos \sqrt{\frac{\gamma - 1}{\gamma + 1}} \cdot \theta \right)^{2\gamma/(\gamma-1)} \tag{11}$$

The pressure along this same streamline is calculated according to the equation holding for the interior region, which with the Bernoulli equation

$$\tfrac{1}{2}U^2 + \frac{D^2}{\gamma - 1} \left[\left(\frac{P}{P_1} \right)^{(\gamma-1)/\gamma} - 1 \right] = \tfrac{1}{2}D^2 \tag{12}$$

is for pressure

$$r^4 = \frac{\left(\dfrac{P_1}{P} \right)^{2/\gamma}}{\dfrac{\gamma + 1}{\gamma - 1} - \dfrac{2}{\gamma - 1} \left(\dfrac{P}{P_1} \right)^{(\gamma-1)/\gamma}} \tag{13}$$

The two pressures so calculated are in general different. Then s_0 is so chosen that the closest agreement is obtained between the two pressures, over a distance along the axis of about one charge radius. The value so found turns out to be $s_0/R = 0.46$, so that the dividing streamline begins 46 per cent of the distance from the surface toward the axis. Figure 10 shows the kind of agreement obtained with this choice of s_0.

With the above choice of streamline, the equations for determining the expansion as a function of reaction zone length become numerically

$$r = 1.85 \left(1 - \frac{a}{R} \operatorname{ctn} \theta \right) \tag{9b}$$

$$\frac{a}{R} = 0.92 \frac{\sin \theta}{1 + \cos \sqrt{2} \theta} \tag{7c}$$
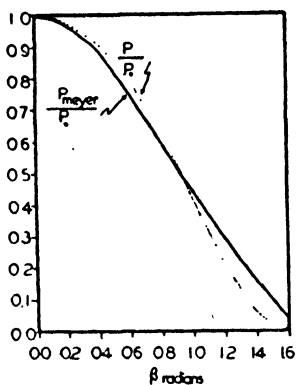
FIG. 10 Match to Meyer solution

Equations 6, 7c, and 9b now determine completely D/D_i as a function of a/R; and the results are given in table 1. The application of this theory to experimental data will be postponed to a later section.

Wilkinson has applied this same method to a lightly cased charge. The only difference is that the solution in the outer region is the Meyer solution for flow around a curved surface, the shape of the surface being calculated and depending on the mass of the casing.

Wilkinson's calculations are given in table 2, for two different values of the ratio weight of case/weight of explosive. The application of these results will likewise be postponed to a later section.

(c) The cased charge

In order to find the radial expansion for a cased charge, consider an idealized casing of negligible strength which is a thin (but possibly heavy) sheath. The equation of motion of the casing under the pressure P is

$$\sigma R \frac{d^2 r}{dt^2} = Pr \tag{14}$$

where σ is the mass per unit area of casing. Upon changing the time derivative to a space derivative, and introducing the ratio W_c/W_e, defined by

$$\frac{W_c}{W_e} = \frac{2\pi R \sigma}{\pi R^2 / V_0}$$

the equation of motion of the case becomes

$$\frac{d^2 r}{dx^2} = 2 \frac{PV_0}{D^2} \frac{1/R^2}{W_c/W_e} r \tag{15}$$

Of the quantities on the right of equation 15, both P and r are variable along the reaction zone, other quantities being constant. Jones first proposed to solve

TABLE 1

a/R	r	D/D_i
0.3	1.0044	0.9806
0.4	1.0120	0.9491
0.5	1.0245	0.9022
0.6	1.0418	0.8451
0.7	1.0626	0.7863
0.8	1.0869	0.7270
0.9	1.1192	0.6621

TABLE 2

$W_c/W_e = 2/3$			$W_c/W_e = 4/3$		
a/R	r	D/D_i	a/R	r	D/D_i
0.3	1.0044	0.9806	0.3	1.0044	0.9806
0.4	1.0109	0.9535	0.4	1.0099	0.9578
0.5	1.0194	0.9206	0.5	1.0194	0.9206
0.6	1.0318	0.8770	0.6	1.0277	0.8909
0.7	1.0466	0.8305	0.7	1.0408	0.8482
0.8	1.0627	0.7857	0.8	1.0562	0.8032
0.9	1.0869	0.7274	0.9	1.0728	0.7603

this general problem by numerical integration. Later he integrated the equation directly for P constant and r variable, but this solution would not seem to correspond closely to the physical situation, for P falls to one-half its initial value while r is changing by only a few per cent. The simplest solution is to consider *all* quantities on the right to be constant (or to have their average values) upon which the solution is:

$$r = 1 + \frac{\bar{P}V_0}{D^2} \frac{(a/R)^2}{W_c/W_e} \tag{16}$$

With this expression for the expansion, the detonation velocity according to equation 6 is approximately

$$\frac{D_i^2}{D^2} = 1 + 9 \frac{\bar{P}V_0}{D^2} \cdot \frac{(a/R)^2}{W_c/W_e}$$

or

$$\frac{D_1^2}{D^2} \approx 1 + 2.5 \frac{(a/R)^2}{W_c/W_e} \tag{17}$$

which is a result obtained by Jones.

The application of this result to experimental data will be postponed to a later section.

(d) The charge with very thick casing

When the casing surrounding an explosive charge is too thick (as when the casing is an extended block of metal), the simple lamina theory does not apply
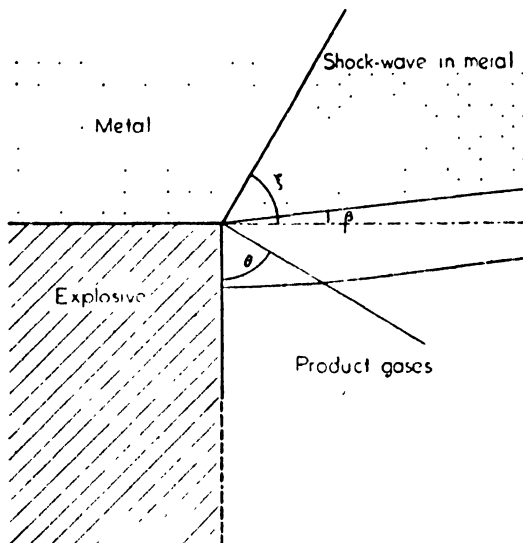
Fig. 11. Jones's construction for metal-sheathed charges

Jones and Strickland have developed a theory which finds the expansion by considering the propagation of a shock wave into the metal surrounding the charge.

Figure 11 presents the geometry of the cylindrical charge expanding as it sets up a shock wave in the surrounding metal. The conditions we seek to satisfy are that (i) the component of material velocity be normal to the shock front and (ii) the pressure match both at the boundary of the expanding charge and at the metal. When by the use of these matching conditions, we have found the angle of expansion β, then the relative expansion at the end of the reaction zone a is given at once by

$$r = 1 + \frac{a}{R} \tan \beta \tag{18}$$

In order to accomplish the matching, first consider the relation between the pressure in the case P_c (all quantities pertaining to the case will be denoted by the subscript c) and the expansion angle β. The angle at which the shock wave

in the metal is propagated is given by

$$\sin \xi = \frac{D_c}{D} \qquad (19a)$$

This may also be written in the form

$$\sin^2 \xi = \left(\frac{P_1 V_0}{D^2}\right)\left(\frac{D_c^2}{P_c V_{0c}}\right)\left(\frac{V_{0c}}{V_0}\right)\frac{P_c}{P_1} \qquad (19b)$$

in which the first factor in brackets is a property of the explosive and is equal to

$$\frac{P_1 V_0}{D^2} = \frac{1 - \alpha/V_0}{\gamma + 1}$$

The second quantity in brackets is a property of the metal, depending on the pressure:

$$\frac{P_c V_{0c}}{D_c^2} = 1 - \frac{V_c}{V_{0c}}$$

where

$$\frac{V_c}{V_{0c}} = 1 - A^2/2B \cdot \ln\left[1 + \frac{2B}{A} P_c\right]$$

is used as the equation of state of the metal.

The third quantity in brackets is the initial density ratio. Thus equation 19b determines the angle ξ as a function of P_c/P_1.

The matching of the normal component of material velocity requires that

$$D \sin \beta = W \cos (\xi - \beta) \qquad (20a)$$

which with the aid of the shock relation

$$\frac{W_c}{D_c} = 1 - \frac{V_c}{V_{0c}}$$

is trigonometrically equivalent to

$$\frac{\tan (\xi - \beta)}{\tan \xi} = \frac{V_c}{V_{0c}} \qquad (20b)$$

Thus the pair of equations (19b and 20b) gives the relation between P_c/P_1 and expansion angle β for any particular casing substance, and several such curves are given in figure 12 (from Jones and Strickland's paper).

Next it is necessary to consider the relation between pressure and expansion within the product gases. The products are once more supposed to obey the polytrope $PV^3 = $ const. and to expand according to the Meyer streamlines up to a region within the angle θ, at which point the pressure is constant; thereafter the streamlines are straight lines at the angle β to the axis. The pressure along this Meyer streamline is

$$\frac{P_{\text{Meyer}}}{P_1} = \cos^3 \frac{\theta}{\sqrt{2}} \qquad (21)$$

and the angle of expansion β of the Meyer streamline is given by

$$\tan(\theta - \beta) = \sqrt{2} \cdot \tan \frac{\theta}{\sqrt{2}} \tag{22}$$

The pair of equations (21 and 22) gives the relation between P_{Meyer}/P_1 and expansion angle β for any explosive with the polytropic exponent 3, suitably TNT. This curve is also drawn in figure 12. Since the required matching condition is that $P_c = P_{\text{Meyer}}$, the intersections of these lines give the desired expansion angles β. The results obtained by Jones and Strickland are listed in table 3. These results, together with equations 18 and 6, determine the detonation
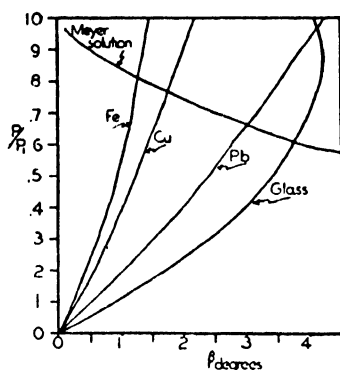
FIG. 12. Shock pressures for various sheaths

TABLE 3

SUBSTANCE	β
TNT in copper. . .	1° 46′
TNT in iron .	1° 18′
TNT in lead	3° 3′
TNT in glass	3° 48′
TNT in bakelite	10° 40′

velocity as a function of a/R for a heavy-cased charge of any particular explosive and casing material.

(e) Assembled results

Since each of the studies of the expansion of a finite charge leads to a relation between the ratio D/D_1 and the ratio a/R, the results may all be presented on a single graph, and this has been done in figure 13.

This figure may in fact be used as a convenient working diagram for the application of the nozzle theory to experimental data, in lieu of using the algebraic expressions in equations 6, 7c, 9b, 17, and 18. It is only necessary to enter the diagram at the appropriate values of D/D_1 and W_c/W_e, and to read the corresponding value of a/R. The actual application of this theory to experimental

data will be postponed until after the presentation of the curved-front theory of the detonation velocity of finite charges.

3. *The curved-front theory*

(a) The effect of curvature

The alternative theory of the finite charge begins with the assumption that any small portion of the actual detonation wave can be approximated by a spherical detonation wave. It is therefore necessary to find the effect of curvature of a detonation front upon its velocity.

We first write the four hydrodynamic-thermodynamic equations: continuity, motion, energy, and Chapman–Jouguet. If the detonation front be a sphere of radius of curvature r_0, the differential equation of continuity is, if a steady state
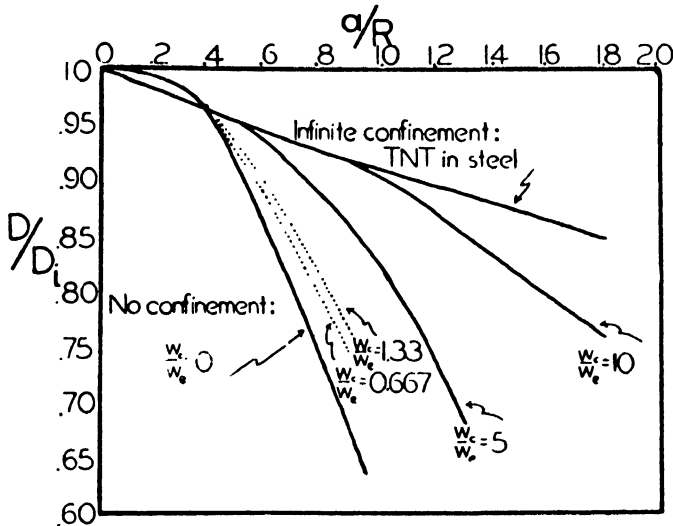
Fig. 13. Characterizing chart for nozzle theory

be assumed:

$$(D - W)\frac{dV}{dr} = -\frac{2VW}{r} - V\frac{dW}{dr} \tag{23a}$$

This is also equation B5 of appendix B. Upon integration, this becomes

$$\frac{D - W}{V} = \frac{D}{V_0} - 2\int_{r_0}^{r_0-a}\frac{W}{Vr}\,dr \tag{23b}$$

or with the notation $U \equiv D - W$ and the notation

$$\vartheta \equiv 1 + \frac{2V_0}{D}\int_{r_0}^{r_0-a}\frac{W}{Vr}\,dr \tag{24a}$$

the equation of continuity may be written

$$\frac{U}{D} = \frac{V}{V_0}\vartheta \tag{23c}$$

The defining equation for ϑ now becomes

$$\vartheta = 1 - 2 \int_{r_0}^{r_0-a} \frac{\dfrac{V_0}{V} - \vartheta}{r} \, dr \tag{24b}$$

or making the approximation of taking the integrand outside the sign of integration

$$\vartheta \approx 1 - 2 \left(\frac{V_0}{V_1} - 1 \right) \frac{a}{r_0} \tag{24c}$$

If V_1/V_0 has the numerical value 0.8 appropriate to solid explosives,

$$\vartheta = 1 - 0.5 \frac{a}{r_0} \tag{24d}$$

In the practical evaluation of ϑ, equation 24d will be used.

The differential equation of motion is

$$V dP + U dU = 0 \tag{25}$$

just as for the plane detonation. Although this equation cannot be integrated exactly, it can be integrated approximately by substituting for U and dU their values obtained from the continuity equation 23c:

$$dP + \frac{D^2}{V_0^2} V \vartheta d\vartheta + \frac{D^2}{V_0^2} \vartheta^2 dV = 0 \tag{26a}$$

which upon integration becomes

$$P + \frac{1}{2} \frac{D^2}{V_0^2} \vartheta^2 V + \frac{1}{2} \frac{D^2}{V_0^2} \int \vartheta^2 dV = \text{const.} \tag{26b}$$

Since most of the contribution to the integral in equation 26b will be near $\vartheta = 1$, we make the approximation of assigning it that value, whereupon the equation of motion becomes

$$P + \frac{U^2}{V} \frac{1 + \vartheta^2}{2\vartheta^2} = \frac{D^2}{V_0} \tag{26c}$$

The differential equation of energy is

$$dE + d(PV) + U dU = dQ \tag{27a}$$

just as for the plane wave, and its integrated form can be written down at once

$$\Delta E + PV + \tfrac{1}{2} U^2 = \Delta Q + \tfrac{1}{2} D^2 \tag{27b}$$

or for an imperfect gas such that $P(V - \alpha) = RT$,

$$\frac{1}{\gamma - 1} P(V - \alpha) + PV + \tfrac{1}{2} U^2 = \Delta Q + \tfrac{1}{2} D^2 \tag{27c}$$

The Chapman–Jouguet condition is, if the wave front is not too strongly curved,

identical with that for the plane wave:

$$U_1^2 = \frac{P_1 V_1^2 \gamma}{V_1 - \alpha} \tag{28}$$

We return later to the situation which will hold for waves of small radii of curvature: namely, that the simple Chapman–Jouguet condition does not hold.

Upon combining the four hydrodynamic-thermodynamic equations (23c, 26c, 27c, and 28), and recalling that the detonation velocity D_i of an ideal plane wave in an imperfect gas is

$$D_i^2 = 2(\Delta Q + \bar{C}_v T_0) \frac{(\gamma^2 - 1)}{\left(1 - \frac{\alpha}{V_0}\right)^2} \tag{I:6d}$$

we obtain without approximations the final relation between detonation velocity and the parameter ϑ:

$$\frac{D_i^2}{D^2} = \left[\frac{\gamma + 1}{1 + \gamma \frac{1 + \vartheta^2}{2\vartheta^2}} \right]$$

$$\cdot \left[1 + \frac{1 - \vartheta^2}{\vartheta^2} \left\{ \frac{\gamma^2 \left(1 - \frac{\alpha}{V_0}\right) + \frac{\gamma}{2}\left(1 - \frac{\alpha\vartheta^2}{V_0^2}\right) - \frac{\gamma^2}{4}(\gamma - 1)\left(\frac{1 - \vartheta^2}{\vartheta^2}\right)}{\left(1 - \frac{\alpha}{V_0}\right)^2 \left(1 + \gamma \frac{1 + \vartheta^2}{2\vartheta^2}\right)} \right\} \right] \tag{29}$$

The volume at the end of the reaction zone is also found to be:

$$\frac{V_1}{V_0} = \frac{\frac{\gamma}{\vartheta^2} + \frac{\alpha}{V_0}}{1 + \gamma \frac{1 + \vartheta^2}{2\vartheta^2}} \tag{30}$$

Values computed from equation 29 with equation 24d are listed in table 4.

When the radius of the spherical wave is of the order of one reaction zone length, and a fortiori for smaller radii, it is necessary to make use of the generalized Chapman–Jouguet condition as discussed in appendix B. We first determine the Chapman–Jouguet point for a wave whose radius of curvature is r_0. The Chapman–Jouguet point is where the rate of pressure increase due to reaction is exactly equal to the rate of pressure loss due to curvature; thus where

$$\left(\frac{\partial P}{\partial N}\right)_v \frac{dN}{dt} = \frac{2s^2 W}{V r_0} \tag{31}$$

We now approximate the derivatives in equation 31:

$$\left(\frac{\partial P}{\partial N}\right)_v \approx P_1 \tag{32}$$

$$\frac{dN}{dt} \sim \frac{1}{\tau} \tag{33}$$

Here τ is the time spent by the particle in the reaction zone, and is related to the reaction zone length a by

$$\tau = \int \frac{dr}{U} \approx \frac{V_0}{V_{1r}} \frac{a}{D} \tag{34}$$

(Note that the reaction time τ is greater (by about 25 per cent) than the time required for the reaction zone to pass a stationary observer. This is because the reacting particle has a velocity in the same direction as the velocity of propagation.)

With these substitutions, together with the continuity equation and the definition of sound velocity, equation 31 gives:

$$\frac{a}{r_0} = \frac{V_{1r}(V_1 - \alpha)}{2V_1(V_0 - \vartheta V_1)} \tag{35a}$$

TABLE 4

r_0/a	D_{r_0}/D_i	r_0/a	D_{r_0}/D_i
1	0.638 (?)	7.5	0.874
1.25	0.625	10	0.902
1.75	0.662	15	0.932
2.5	0.721	20	0.948
5	0.826	40	0.974

TABLE 4A

r_0/a_i	D_{r_0}/D_i	r_0/a_i	D_{r_0}/D_i
1.5	0.627	0.50	0.362
1.25	0.573	0.25	0.256
1.0	0.512	0	0
0.75	0.444		

For numerical solution, it is necessary to solve this equation simultaneously with equations 30 for V_1 and 24d for ϑ. The result is

$$\frac{a}{r_0} = 0.616 \tag{35b}$$

It is now possible to extend table 4 to smaller radii, if it be assumed that the detonation velocity is approximately proportional to the square root of the fraction of material reacting in the "reaction zone". Thus,

$$\frac{D}{D_i} \approx \frac{D_{r_0 = a_i/0.616}}{D_i} \sqrt{\frac{a}{a_i}} = 0.652 \sqrt{\frac{0.616 r_0}{a_i}} \tag{36}$$

The results of tables 4 and 4a are plotted in figure 14; the curve is composed of two portions, the reaction being progressively less complete in the region of small radii (represented by a dashed line on the figure). The relation between

detonation velocity and curvature expressed in figure 14 is the foundation for the remainder of the curved-front theory of finite charges.

(b) The uncased charge

It will be assumed that the wave front in a detonation propagating along a charge of finite radius is meniscus-shaped; and further, that any small portion of this meniscus can be satisfactorily approximated by a segment of a steady spherical wave. This means that if the forward velocity of the detonation wave is
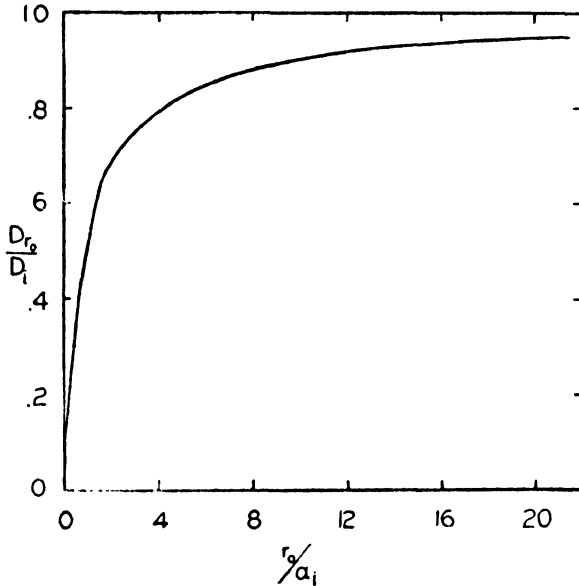
Fig. 14. Detonation velocity vs. curvature of wave front

D and the angle between the axis and the normal to a point on the wave front is ϕ, the radial velocity of the wave front at that point is

$$D_{r_0} = D \cos \phi \tag{37}$$

and the curvature of the wave front at that point is read (in units of a) from figure 14.

It is now possible by a step-by-step graphical construction to find the shape of a detonation front for any desired value of D/D_i. Thus for the first 10° of arc the front is constructed with a radius read from figure 14, with D_{r_0}/D_i taken to be $D/D_i \cos 5°$; for the second 10° of arc, the corresponding velocity is $D/D_i \cos 15°$; and so on until an angle of 90° has been reached, it being assumed that for an uncased charge the wave front will reach the surface at this angle. The ratio reaction zone length a/radius of charge R is now measured on the drawing. An example of the method of construction is given in figure 15.

In the region of high curvature which should exist near the surface of the

charge, the reaction will be progressively less complete. However, it is just in this region that the interactions of neighboring elements of fluid become important, so that the assumptions of the treatment are no longer valid. Therefore the position of this zone of incomplete reaction cannot be specified with any real precision.

This graphical construction has been carried through for a series of values of D/D_i, and the corresponding values of a/R are given in table 5 and in figure 16. Since the curves constructed to compute table 5 are of some interest in themselves, as giving the shape of wave fronts calculated by this theory, they are reproduced in figure 16.

AXIS OF CHARGE a
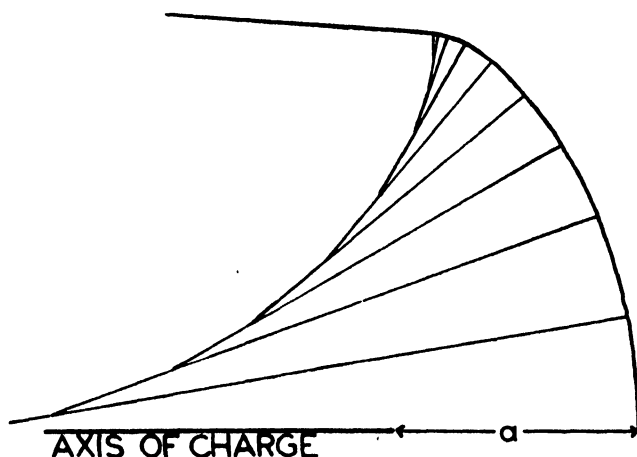
FIG. 15. Construction of wave front

TABLE 5

a/R	D/D_i	a/R	D/D_i
0	1	0.40	0.80
0.11	0.95	0.52	0.70
0.20	0.90	0.68	0.70
0.29	0.85	0.82	0.65

The data of figure 17 are represented with considerable faithfulness by the empirical equation:

$$\frac{D}{D_i} = 1 - 0.5 \frac{a}{R} \tag{38}$$

Equation 38 will be used for the application of the theory to experimental data, which will be postponed to a later section.

(c) The cased charge

Consider a cased charge and assume that the confining action is due to the inertia of the case. It can now be assumed that the meniscus-shaped detonation

front adjusts itself to such an angle ϕ of intersection with the case that the elements of the case move away neither faster nor slower than the elements of fluid in contact with it, both moving in the direction normal to the wave front at the
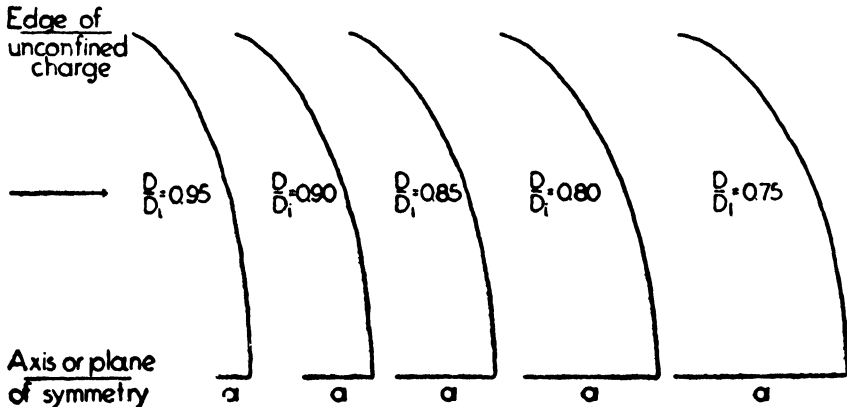
FIG. 16. Wave fronts for various reaction zone lengths
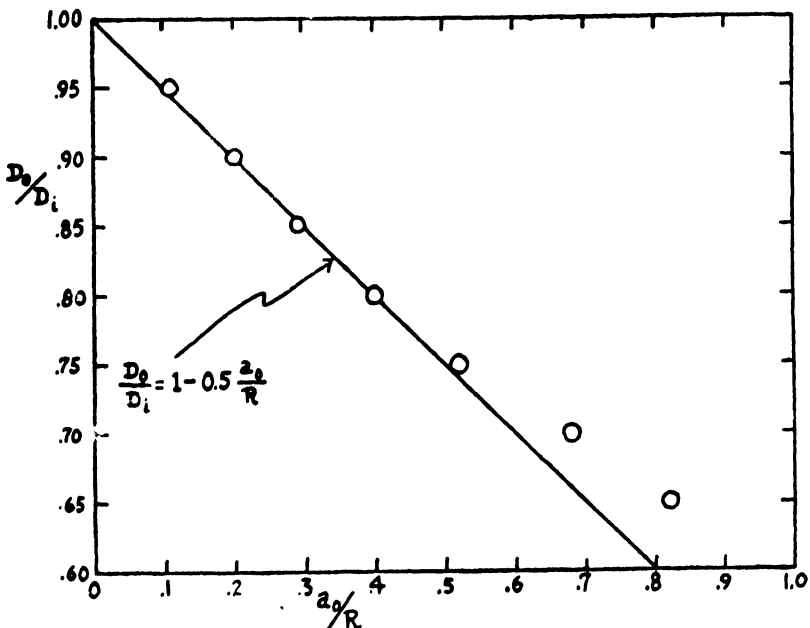
FIG. 17. Justification curve for approximation: infinitely thick casing

point of intersection. Then the momentum delivered to unit area of the case is approximately $\sigma W_1 \sin \phi$, and this is produced by a pressure of approximately P_1 acting for a time τ. Thus

$$P_1 \tau = \sigma W_1 \sin \phi \qquad (39a)$$

Upon substituting for P_1 and W_1 their values for the ideal wave, for τ in terms of a, and for σ in terms of W_c/W_e, this becomes

$$\sin \phi = 2 \frac{V_0}{V_1} \frac{a/R}{W_c/W_e} \tag{39b}$$

or numerically

$$\sin \phi \approx 2.5 \frac{a/R}{W_c/W_e} \tag{39c}$$

Now it is only necessary to use the curves constructed in figure 16, but considering the surface of the charge to be at the point where ϕ is given by equation 39c. Numerical values so computed are given in table 6 and in figure 18.

TABLE 6

SIN ϕ	$(a/R)^2/(W_c/W_e)$		
	$D/D_i = 0.95$	$D/D_i = 0.90$	$D/D_i = 0.85$
0.065	0.017		
0.075	0.017		
0.10	0.020	0.044	
0.15	0.020	0.042	0.066
0.20	0.020	0.043	0.066
0.25	0.020	0.044	0.068
0.30	0.021	0.045	0.071
0.35	0.022	0.045	0.070
0.40	0.024	0.047	0.073
0.45	0.024	0.050	0.076

The data of figure 18 are represented with reasonable fidelity by the empirical equation

$$\frac{D}{D_i} = 1 - 2.17 \frac{(a/R)^2}{W_c/W_e} \tag{40}$$

Equation 40 will be used later for the application of the theory to experimental data.

(d) The charge with very thick casing

Consider a cased charge and assume that the confining action is due to the setting up of a shock wave in the case, and that the meniscus-shaped detonation front adjusts itself so that the pressure and the particle velocity match at the boundary of the charge.

If the detonation front at the boundary is moving with the local velocity D_r at an angle ϕ with the axis, and the shock wave in the case has the velocity D_c at the angle ϕ_c, these are given by

$$D_r = D \cdot \cos \phi \tag{41}$$

$$D_c = D \cdot \cos \phi_c \tag{42}$$

The requirements that the pressures must match at the boundary and that the particle velocities must match at the boundary are written

$$P_{1c} = P_{1r} \tag{43}$$

$$W_{1c} \sin \phi_c = W_{1r} \sin \phi \tag{44}$$
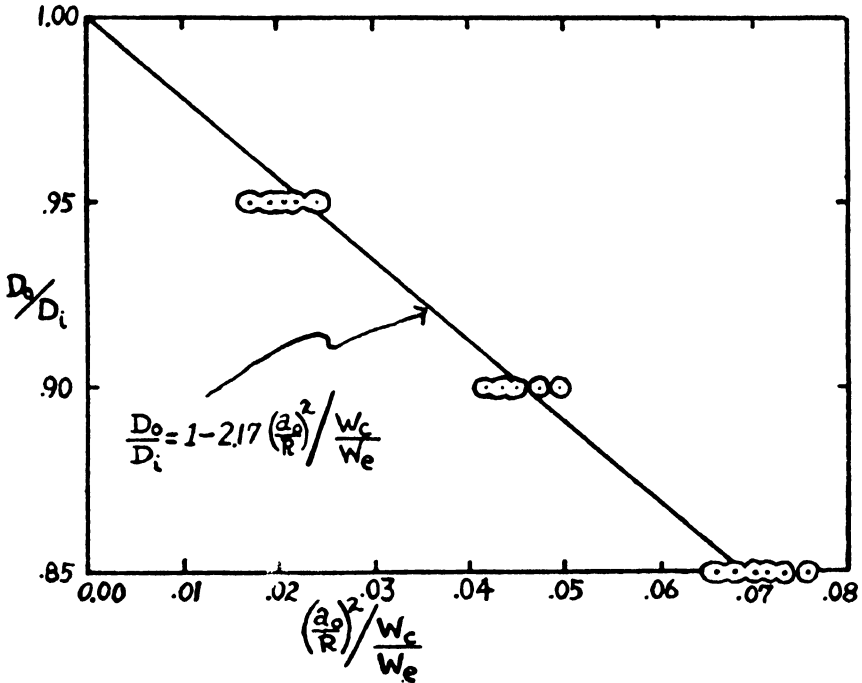
FIG. 18. Justification curve for approximation: heavily cased charges

The shock conditions in the explosive and in the case respectively are

$$P_{1r}V_0 = W_{1r}D_r \tag{45}$$

$$P_{1c}V_{0c} = W_{1c}D_c \tag{46}$$

When the preceding six equations are combined, they yield

$$\tan \phi = \frac{V_{0c}}{V_0} \sqrt{\frac{D^2}{D_c^2} - 1} \tag{47}$$

If the velocity D_c of the shock wave in the case has been measured, equation 47 gives at once the angle at which the wave front intersects the case.

If, as is more usual, the shock wave velocity has not been measured, it must be calculated from the sonic velocity C in the case and the equation of state of the case material.

For velocities not far above sonic, the velocity of a shock wave in a solid is given approximately by

$$\frac{D_c}{C} = 1 + AP \tag{48}$$

where A is the compressibility of the solid. With the pressure given by

$$P = \frac{D^2 \cos^2 \phi}{V_0} \cdot \frac{1 - \alpha/V_0}{1 + \gamma} \tag{49}$$

a few iterations of equations 49, 48, and 47 will easily give the value of D_c and so of the angle ϕ.

When the angle ϕ is known, it is only necessary to use the curves constructed in figure 16 to determine a/R. Numerical values so computed are given in table 7 and in figure 19.

TABLE 7

SIN ϕ	$\frac{a}{R}$ SIN ϕ		
	$D/D_i = 0.95$	$D/D_i = 0.90$	$D/D_i = 0.85$
0.04	0.053		
0.05	0.045		
0.065	0.042		
0.075	0.043		
0.10	0.050	0.109	
0.15	0.050	0.104	0.165
0.20	0.048	0.107	0.164
0.25	0.051	0.111	0.171
0.30	0.052	0.112	0.178
0.35	0.054	0.112	0.175
0.40	0.059	0.118	0.183
0.45	0.061	0.124	0.190

The data of figure 19 are represented with reasonable fidelity by the empirical equation

$$\frac{D}{D_i} = 1 - 0.88 \frac{a}{R} \sin \phi \tag{50}$$

Equation 50 will be used later in the application of the theory to experimental data.

(e) Assembled results

The relations between D/D_i and a/R for uncased, cased, and heavily cased charges may all be presented on a single graph, and this has been done in figure 20. This figure may in fact be used as a convenient working diagram for the application of the curved-front theory to experimental data, in lieu of using the algebraic expressions in equations 38, 40, and 50. It is only necessary to enter
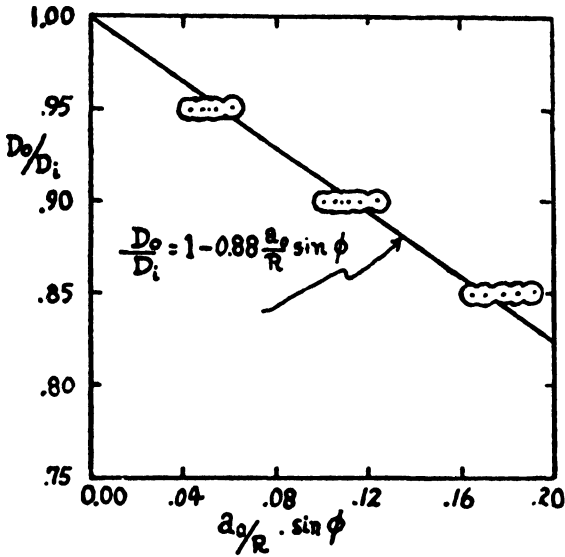
FIG. 19. Justification curve for approximation: lightly cased or unconfined charges
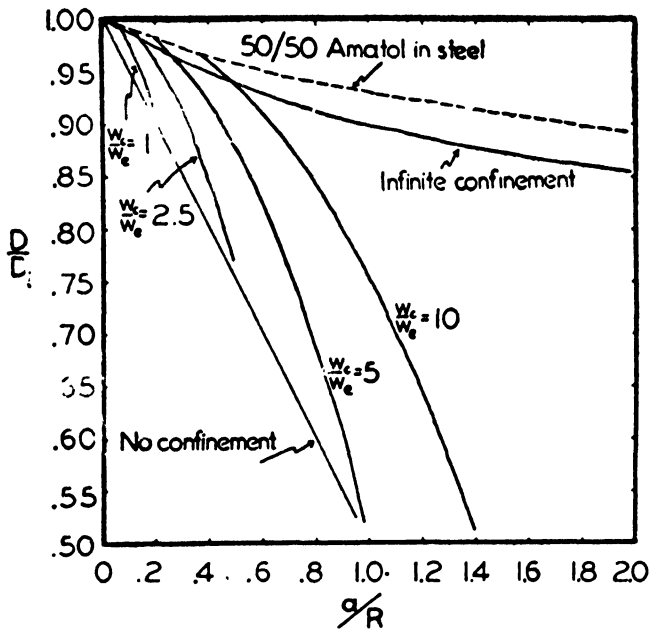
FIG. 20. Characterizing chart for cased charges

the diagram at the appropriate values of D/D_i and W_c/W_e, and to read the corresponding value of a/R.

The reader will notice the similarity of the final results of this theory to those of the nozzle theory (figure 13).

4. Critique of the theories

Hydrodynamic assumptions common to both theories: In the development of both theories it is assumed that the only perturbation on the hydrodynamic equations is on the continuity equation; this means in particular that no transport of momentum or of energy out the edges of the charge is considered. This simplification makes the hydrodynamic equations tractable enough to permit
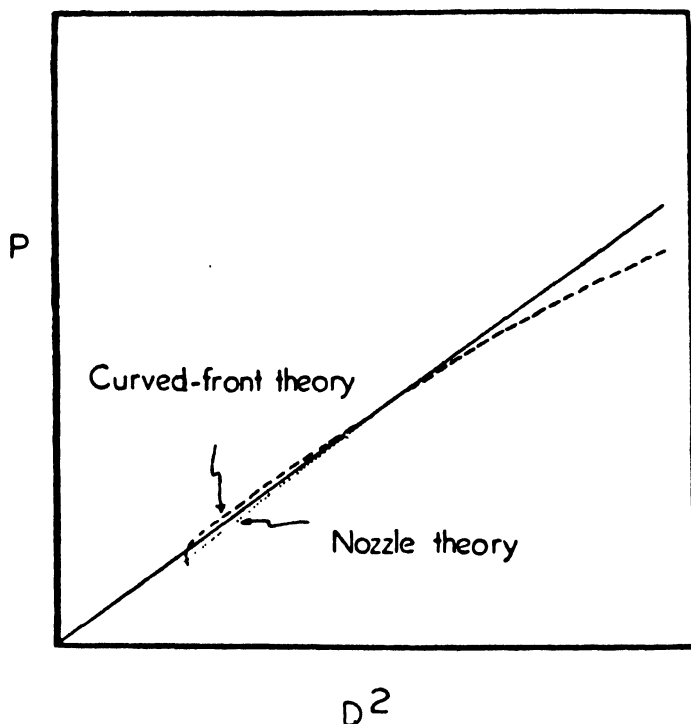
Fig. 21. Comparison between nozzle and curved-front theories

their solution; and in view of the comparatively low lateral velocities, the simplification seems to be an acceptable one. Nevertheless, it would be desirable in a further theoretical treatment to make some explicit allowance for the loss of momentum and energy (as well as material) laterally.

There is a possibility of attacking the problem by a direct experimental method; this is to measure the material velocity W for various finite sticks by the x-ray "zebra-charge" method, and then to compare the measured ratio W/D with that predicted by the theories. However, the effect of the perturbation is in any event small, and may well be undetectable within the accuracy of the x-ray method.

As a result of the initial assumption that only the continuity equation is perturbed, it turns out that in the final results of both theories, the relation of P to D (and to W) is very close to that for the ideal plane wave. This is demonstrated in figure 21, which presents the P,D relation according to the respective theories, together with the F,D relation for an ideal plane wave in the same explosive, corresponding to various heats of reaction. (Actually, because of loss of momentum laterally, the points in the P,D plane for $D < D_i$ must lie somewhere *below* the ideal pressure line.)

Because of the neglect of the lateral loss of momentum and energy, it must be remembered that the velocity loss caused by a given expansion (or curvature) will be somewhat underestimated by the present theories. *This is to say that any reaction zone lengths computed by the present theories are to be viewed as possibly high estimates.* There is in fact some evidence obtained by Herzberg and Walker which indicates that the reaction zones may be shorter by a factor of several-fold than would be estimated by the present theories. Thus they obtain from photo-

TABLE 8

EXPLOSIVE	LUMINOUS ZONE
	cm.
RDX-BWX, density 1.56	0.03
Tetryl, density 1.52...	0.07
NENO, density 1.53.	0.07
NENO + 1% graphite, density 1.6	0.08
TNT, density 1.52	0.06
TNT + 5% Al, density 1.6.	0.09
Amatol 55/45, density 1.5.....	0.09

graphs lengths of the luminous zones as given in table 8, which may be contrasted with the longer zones given in a later section of this report.

It may be well to mention in passing that the expansions (and consequent lowerings of velocity) calculated by the nozzle and by the curved-front theory are alternative, not supplementary to one another. The two treatments adopt different means of attaining the same result: namely, finding the flow lines in the reaction zone. It would be quite erroneous to superimpose on the losses computed from the nozzle theory additional losses according to the curved-front theory, or *vice versa*.

Experimental detection of the meniscus-shaped front: One notable result of the theory of finite charges as developed by the present writers is the prediction[15] that the detonation front will be meniscus-shaped.

The shape of the wave front has been investigated by means of high-speed rotating-mirror cameras by two research groups. Herzberg and Walker took

[15] Actually, it had been shown earlier by means of rotating-drum camera pictures of low-density nitroguanidine charges that the wave was indeed meniscus-shaped. However, this experimental observation was not known to Eyring *et al.* at the time the theory was being developed.

photographs of a 16-mm. diameter charge of RDX-BWX, a 16-mm. diameter charge of TNT of density 1.55, and a 55/45 Amatol charge of 31 mm. diameter. They found that for the RDX-BWX the deviation from the plane wave front was less than 0.3 mm.; in the TNT, the bending back near the edge of the detonation front was 0.4 ± 0.2 mm.; and in the Amatol the deviation of the actual wave front from the "geometrical" wave front near the edge of the charge was 3.7 mm.
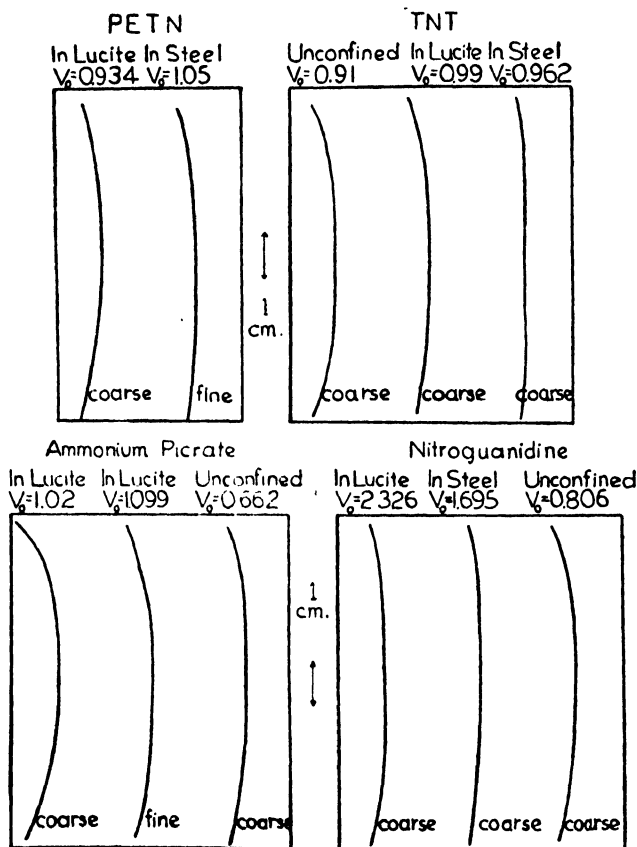
FIG. 22. Experimental wave shapes

Hurwitz and Strecker took head-on rotating-mirror photographs of a number of explosive charges of 65-mm. diameter, and succeeded in finding curved fronts in most instances. The effect is particularly marked with the low-density explosives. Figure 22 reproduces the wave shapes as determined by Hurwitz and Strecker.

This direct experimental evidence for the curvature of the wave front is supporting evidence for the curved-front theory for the velocity in finite charges.

Extrapolated ideal detonation velocities: Inspection of figures 13 and 20 shows

that the chief difference between the final results of the nozzle theory and the curved-front theory lies in that the former obtains a graph for D/D_i vs. a/R which is almost horizontal for small a/R, sloping sharply downward at a/R near unity, while the latter obtains a graph which slopes downward over its whole length. If then a sufficient number of measurements were made over a range of R, it should be possible to choose between the two treatments.

Actually, the experimental data for any one explosive are not sufficient in number or precision to force a decision on this basis. The ideal detonation velocity obtained by extrapolation of data for finite charges according to the curved-front treatment is usually slightly higher than the value measured for very large sticks; while the ideal velocity by extrapolation according to the nozzle treatment is usually lower than the measured value. Of the two, the curved-front treatment gives somewhat more consistent results.

In the analysis of experimental data which will be presented in the next section, the curved-front treatment will be followed.

5. Applications to experimental data

We may now proceed to an analysis of the available data on detonation velocities of finite charges, with the intention of using the theories just developed to find from the measured velocities the corresponding reaction zone lengths.

The data of Parisot and Laffitte (56) and a considerable number of experiments by British and American investigators[16] can be drawn upon. This material has been presented graphically in figures 23–31.

In the instance of cased charges, it is necessary to know whether the casing is to be treated as thin or thick ("characterizing" the charge). To do this one merely plots the experimental data upon the assembled-results diagram of figure 20, entering the diagram with the appropriate D/D_i and W_c/W_e. It then becomes obvious at once whether the experiments fall in the region of thin casing or of infinitely thick casing. Figures 26, 27, and 28 are such "characterizing" plots. Most of the data plotted for Amatol will be seen to fall in the region of moderate confinement, while the data for TNT in steel and Minol 2 in lead clearly fall in the region of infinitely thick confinement.

The reaction zone length a is computed from the slopes of the lines in figures 23–56, according to the equation developed earlier:

$$\frac{D}{D_i} = 1 - \frac{1}{2}\frac{a}{R} \qquad\qquad \text{Uncased} \quad (38)$$

$$\frac{D}{D_i} = 1 - 2.17\frac{a/R}{W_c/W_e} \qquad\qquad \text{Cased} \quad (40)$$

$$\frac{D}{D_i} = 1 - 0.88\frac{a}{R}\sin\phi \qquad\qquad \text{Infinitely cased} \quad (50)$$

---

[16] Among the workers who made important experimental and theoretical contributions in this field are D. P. MacDougall, G. H. Messerly, M. D. Hurwitz, H. A. Strecker, R. W. Cairns, and R. W. Lawrence; also the British workers A. R. Ubbelohde, W. B. Cybulski, J. L. Copp, and others.

In each instance the ideal velocity D_i was included on the figure if known by direct measurement; otherwise the extrapolated value was used. For the infinitely cased charges, the angle ϕ of intersection was for TNT in steel 8°10′ (from the velocity of sound in steel, 5130 m./sec.) and for Minol 2 in lead 20° (from the velocity in lead of a shock produced by Pentolite, 2745 m./sec.).

Figures 23-25 give the experimental vs. theoretical relation for uncased charges, and figures 26-31 that for cased charges.

C. THE TIME-DEPENDENT WAVE

Although every explosive possesses an unique steady-state velocity D_i, it is quite easy to impose upon an explosive charge a velocity either higher than D_i or
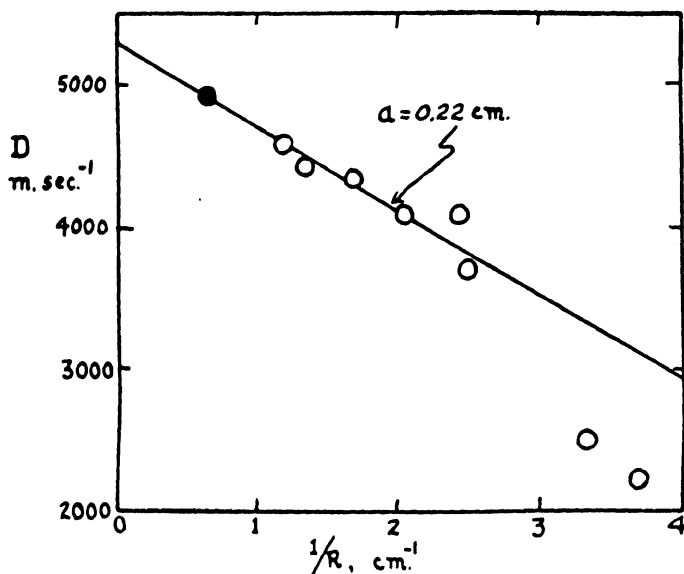
FIG. 23. Reaction zone curve for picric acid in glass. $V_0 = 1.11$ cm.^{3}g.$^{-1}$ ○, Parisot and Laffitte; ●, MacDougall.

lower than D_i. The former will be accomplished by initiating with a high-velocity booster charge, the latter with a low-velocity booster charge. As time goes on, the too high velocity will build down until it reaches the ideal value D_i; likewise, the too low velocity will build up until it reaches the ideal value D_i (unless it is so low that failure occurs).

The fact that any non-steady velocity will approach the steady value should be intuitively obvious. It can, however, be justified more rigorously: Suppose the wave to be initiated above its steady velocity. Then the energy liberated by the chemical reaction is less than sufficient to produce the pressure needed behind the wave front to maintain this high velocity. The velocity must therefore fall. The argument holds also for a wave initiated below its steady velocity, mutatis mutandis.
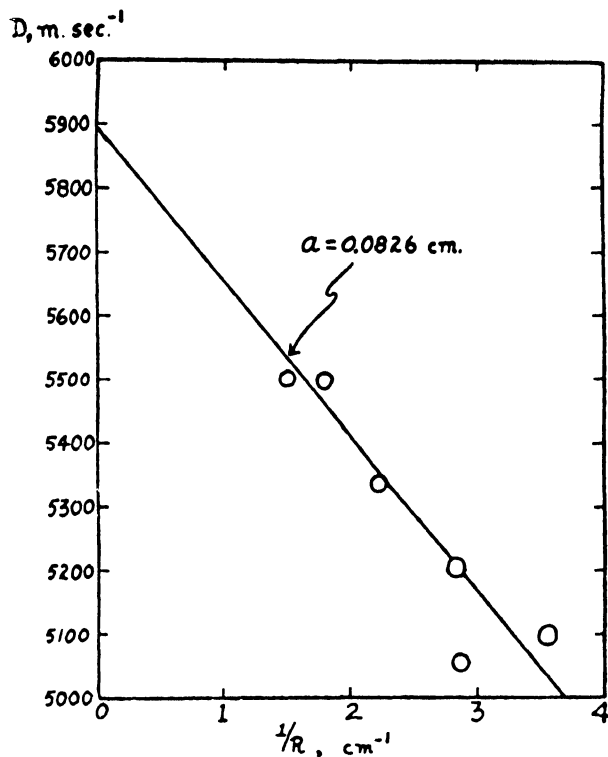
Fig. 24. Reaction zone curve for RDX; $V_0 = 1.11$ cm.^{3}g.$^{-1}$; O, Parisot and Laffitte
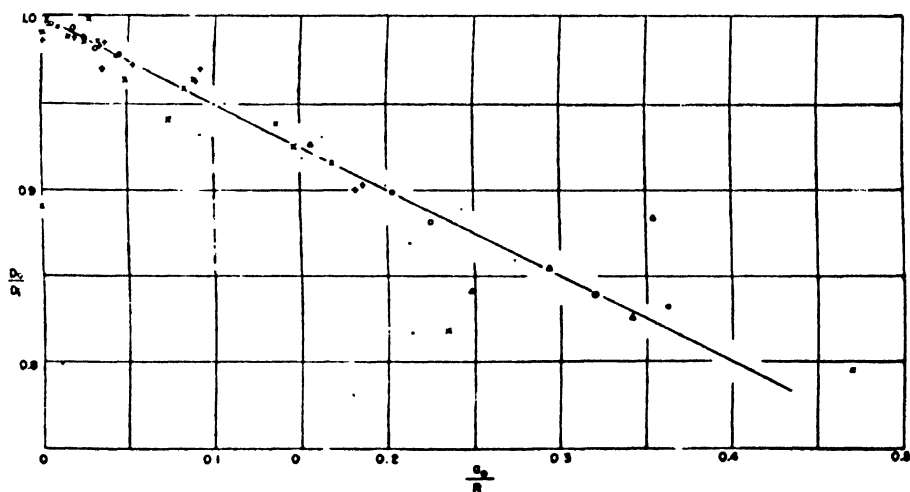
Fig. 25. Dimensionless chart for D vs. R. •, TNT; ×, PETN; +, Tetryl; O, nitroglycerin; ●, ammonium picrate; □, Minol 2; △, 60/40 Amatol; ▲, TNT + 5% Tetryl.
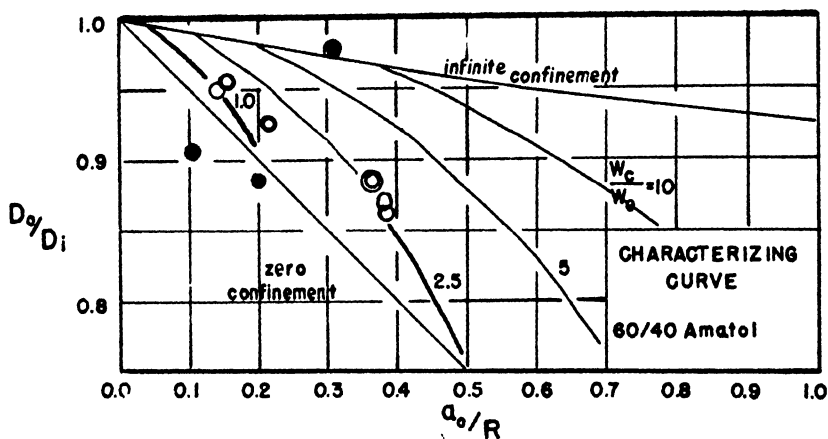
Fig. 26. Characterizing curve for 60/40 Amatol
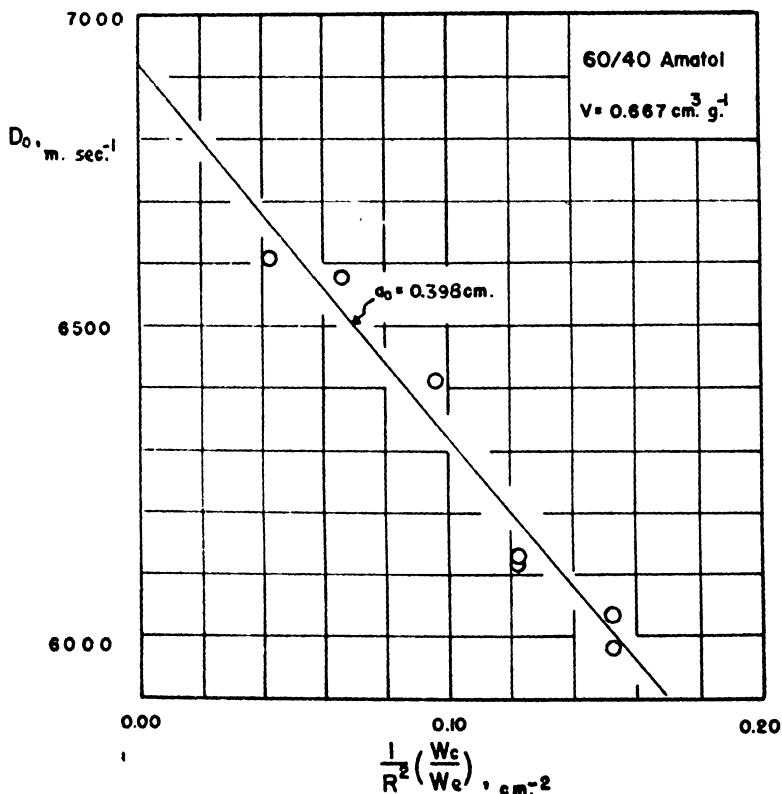
Fig. 27. Reaction zone curve for 60/40 Amatol

The following theory (admittedly somewhat heuristic) has been formulated to give the rate of build-up or build-down of such transient waves.

1. Details of theory

Consider a detonation wave propagating at a velocity not its steady velocity, yet close enough to the steady velocity so that the perturbation may be con-
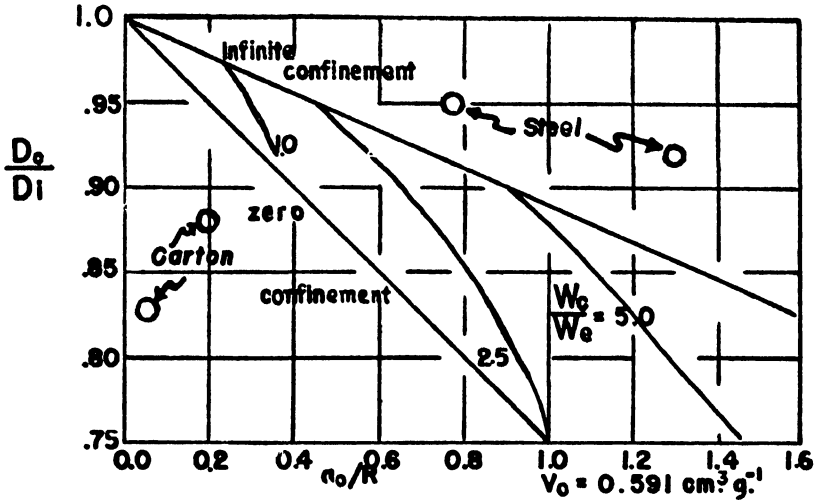
Fig. 28. Characterizing curve for Minol 2 in lead
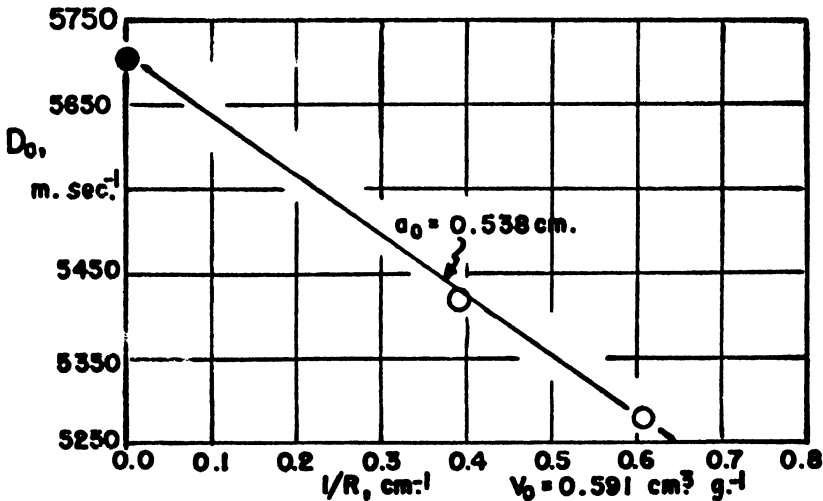
Fig. 29. Reaction zone curve for Minol 2 in lead

sidered small. If we denote the instantaneous velocity at the time of measurement by D, the velocity D_τ a short time τ later will be

$$D_\tau = D + \tau \frac{dD}{d\tau} \tag{51}$$

Now it has been brought out in the discussion of the Chapman–Jouguet condition that the velocity of the detonation front is determined by the values of C and W at the rear of the reaction zone. But of course any changes which occur
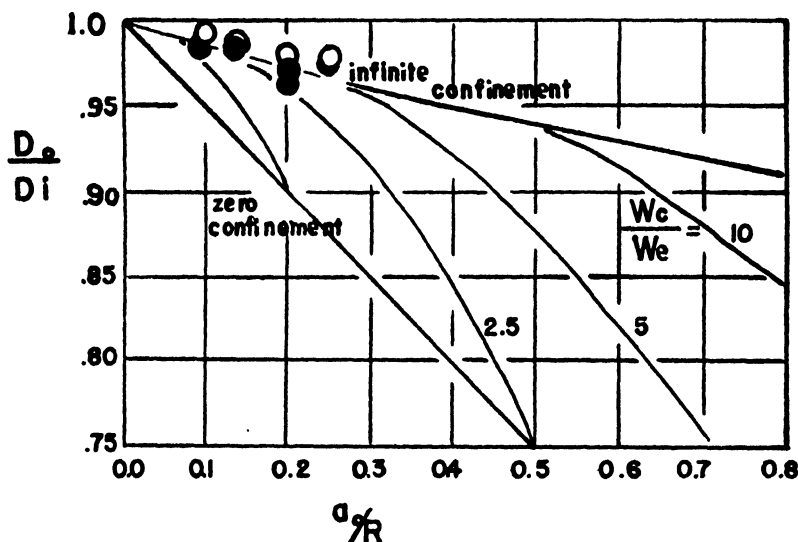
Fig. 30. Characterizing curve for TNT in steel
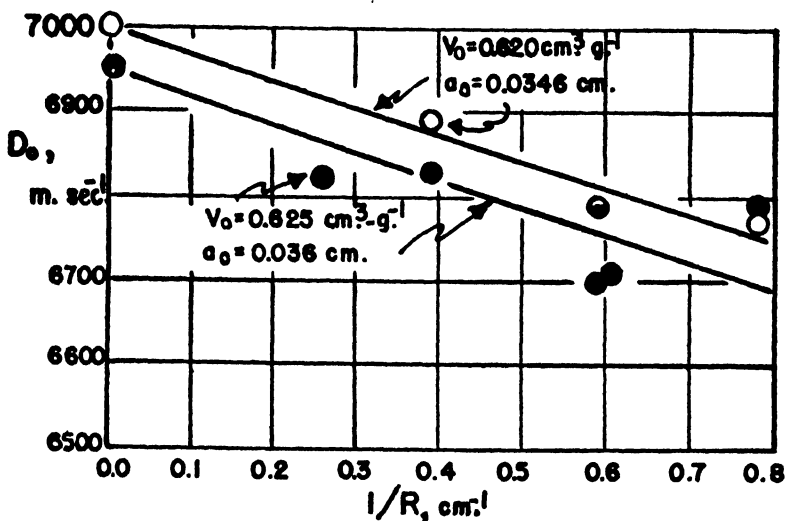
Fig. 31. Reaction zone curve for TNT in steel

at the rear of the reaction zone will not at once make themselves felt at the front of the reaction zone; in fact, the value of C and W at the rear of the reaction zone at a particular instant will determine the velocity of propagation not at that

same instant but at a time τ later where τ is the time required for a signal to traverse the reaction zone, or approximately the reaction time. Thus we write

$$C_1 + W_1 = D_r \tag{52}$$

Upon combining equations 51 and 52 we have

$$\tau \frac{dD}{d\tau} = -D + W_1 + C_1 = -U_1 + C_1 \tag{53}$$

It is necessary to evaluate U_1 and C_1. For this we may use two of the three hydrodynamic-thermodynamic equations (continuity, motion, energy), and we choose for this purpose the two which will be least perturbed by the transient state, so that we can take their steady-state values.

To the extent that the reaction zone length a remains unchanged, as much material flows into the reaction zone as flows out of it, so the continuity equation may be taken in its steady-state form. Since the compression ratio does not involve the heat of reaction, we may even use the same numerical value as for the steady state.

$$\frac{U_1}{D} = \frac{V_1}{V_0} = \frac{\gamma + \alpha/V_0}{\gamma + 1} \tag{54}$$

The differential equation for conservation of energy, $dE + PdV = dQ$, is quite independent of time. To a first approximation, this remains true of its integrated form, so we write as for the steady wave

$$\frac{1}{\gamma - 1} P_1(V_1 - \alpha) + P_1 V_1 + \tfrac{1}{2} U_1^2 = (\Delta Q + \bar{C}_v T_0) + \tfrac{1}{2} D^2 \tag{55}$$

If we now combine the three equations 53, 54, and 55, recalling the definition of C_1 and the value of D_i, and changing the time derivative to a space derivative

$$C_1^2 = \frac{P_1 V_1^2 \gamma}{V_1 - \alpha}$$

$$D_i^2 = 2(\Delta Q + \bar{C}_v T_0) \frac{\gamma^2 - 1}{(1 - \alpha/V_0)^2}$$

$$\tau \frac{dD}{dt} = a \frac{V_0}{V_1} \frac{dD}{dx}$$

we obtain as a final result after a little algebraic manipulation

$$a \frac{dD}{dx} \left(\frac{V_1}{V_0} \right)^2 \left\{ \sqrt{D_i^2 - \frac{1}{2} \frac{(\gamma - 1)[2\gamma + (1 + \lambda)]}{\gamma^2 - \lambda} (D_i^2 - D^2)} - D \right\} \tag{56}$$

which has been presented graphically in figure 32. The calculated points of figure 32 are reproduced with some fidelity by the empirical equation:

$$a \frac{dD}{dx} = 0.333(D_i - D) \tag{57a}$$

Since it was found in Section II that the properties of a detonation wave in a finite stick are very closely the properties of an ideal wave with a smaller heat of

explosion, we can now without significant error extend the treatment to time-dependent waves in finite charges or of spherical shape. It is only necessary to replace the ideal velocity D_i by the steady velocity D_s appropriate to the particular finite charge.

$$a \frac{dD}{dx} = 0.333(D_s - D) \tag{57b}$$

Equation 57b will be used in application of the theory to experimental data.

2. Comparison with theory of pure shock waves: range of validity of the theory

In the derivation of equation 57b, for the transient velocity, it has been assumed (i) that the actual velocity D is not greatly different from the steady velocity D_s, and (ii) that the reaction zone length a remains constant. We may
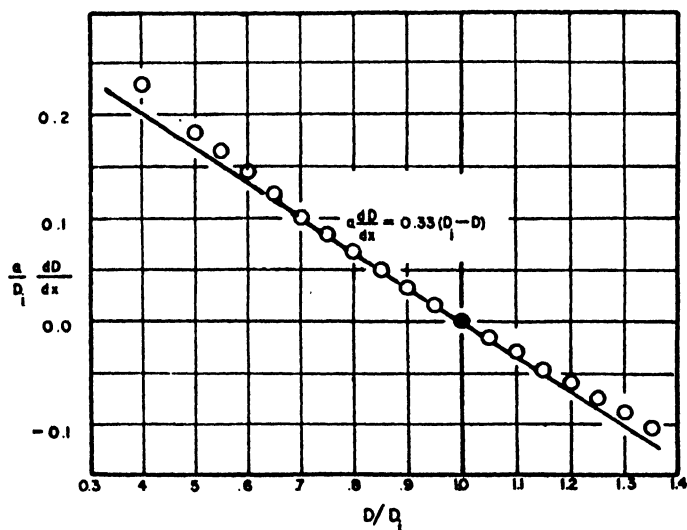
Fig. 32. Justification curve for approximation: building-up or building-down

sometime wish to use equation 57b for a more general transient wave in which D is not near D_s and a is not constant, so it will be useful to know whether the equation breaks down badly under extreme conditions.

To test this point, we may consider a pure shock wave of high intensity, in which no energy at all is supplied by chemical reaction, all the energy of the shock having been supplied at the origin of the wave. In such a wave the "steady" velocity to which it tends is zero (or at most a small sonic velocity); thus $D_s = 0$. Likewise the length of the "reaction zone," or distance to the energy source, is the distance traversed by the wave; thus $a = x$. If equation 57 be supposed valid even under these conditions, then the transient velocity will change with distance as follows:

$$\frac{dD}{dx} \cong - \text{const.} \times \frac{D}{x} \tag{58}$$

The numerical value of the constant in equation 58 would be about 0.33 by the approximate equation 57b, or somewhat smaller (0.12) if computed by equation 57a, for a typical solid explosive with $\gamma = 1.25$ and $\alpha/V_0 = 0.55$. If the explosive were a perfect gas with $\gamma = 1.4$ and $\alpha = 0$, the numerical value of this constant would be about 0.38.

We now compare the result proposed in equation 58 with the results obtained for the transient velocities of pure shock waves by investigators of such waves. One method of analysis of shock waves which vary with time and distance makes use of a rather tedious step-by-step graphical integration of the hydrodynamic equations, making use of the method of characteristics.[17] More convenient for the present purpose is the approximate result in closed form obtained by von Neumann for just the process considered (71). von Neumann finds for a wave of q-dimensional symmetry in a perfect gas

$$D = \frac{2}{q + 2} A^{-2/(q+2)} t^{-q/(q+2)} \tag{59}$$

$$t = A x^{(q+2)/2} \tag{60}$$

where A is a parameter inversely proportional to the square root of the energy supplied. For a shock wave obeying von Neumann's equations 59 and 60, the dependence of velocity on distance is seen to be

$$\frac{dD}{dx} = -\frac{q}{2}\frac{D}{x} \tag{61}$$

For a plane (one-dimensional) wave the numerical coefficient in equation 61 would be 0.5.

The close agreement between equations 58 and 61, extending even to the numerical coefficient, is quite unexpected and surely to some extent fortuitous. Nevertheless, it gives us confidence that equation 58 can be used without significant error over a range of conditions far wider than that for which it was expressly derived.

3. Application to experimental data

Bone and co-workers (11) have published some data on the transient building-down of a detonation in the medium $2CO + O_2$. From their data,

$$D = 2.62 \times 10^5 \text{ cm. sec. }^{-1}$$

$$D_e = 1.76 \times 10^5 \text{ cm. sec.}^{-1}$$

$$dD/dt = -0.427 \times 10^{10} \text{ cm. sec.}^{-2}$$

which with the assumption of a perfect gas of $\gamma = 1.4$ gives a reaction zone length of

$$a = 1.1 \text{ cm.}$$

a value which is reasonable for this gas reaction.

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[17] Reference 3. An application of this method to the expansion of a finite layer of highly compressed gas will be found in the report by W. Döring (23).

Drum-camera photographs have been taken (at Explosives Research Laboratory, Bruceton, Pennsylvania) of a building-up detonation wave in TNT, and of building-down waves in nitroguanidine and in 80/20 Amatol.[18]

The simplest way of determining the reaction zone length from these data is to use the integrated form of equation 57b:

$$\ln (D_s - D) = -\frac{0.333}{a} x + \text{const.} \tag{57c}$$

Thus we may plot graphically $(D_s - D)$ on a logarithmic scale against the distance x on a linear scale, and compute a from the slope of the graph. This has
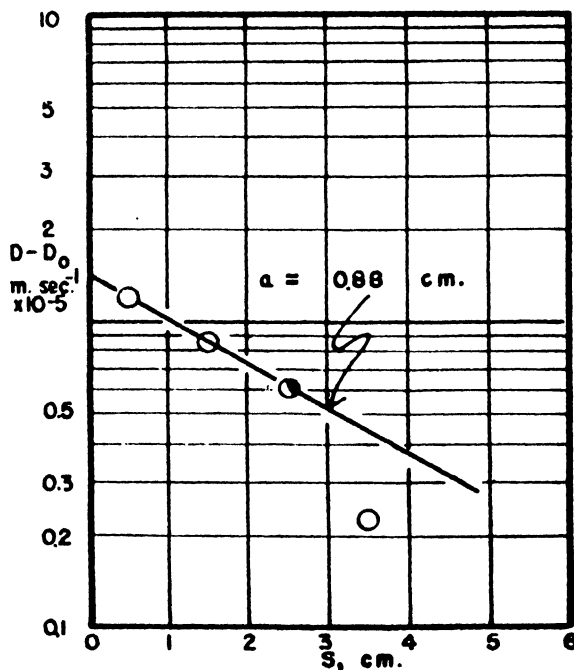
Fig. 33. Reaction zone curve for nitroguanidine. $V_0 = 1.89$ cm.³ g.⁻¹ Photograph No. 3141, Explosives Research Laboratory, Bruceton, Pennsylvania.

been carried through for the TNT, nitroguanidine, and Amatol data in figures 33, 34, and 35. On each diagram is recorded the reaction zone length for the particular explosive studied. These results will be discussed later (Section II E).

It is of some interest to point out that according to the present results, the detonation velocity approaches its steady value exponentially; and further, that the distance in which the difference from the steady value is cut to one-half is approximately two reaction zone lengths.

4. Calculation of transient spherical waves

The rate of change of the detonation velocity of a spherically propagating wave will depend both on its instantaneous velocity D and on its instantaneous

radius of curvature, since $D_s = D_s(r_0/a)$. If it be assumed that the rate of change can be found from equation 57b, and that the appropriate steady velocity D_s can
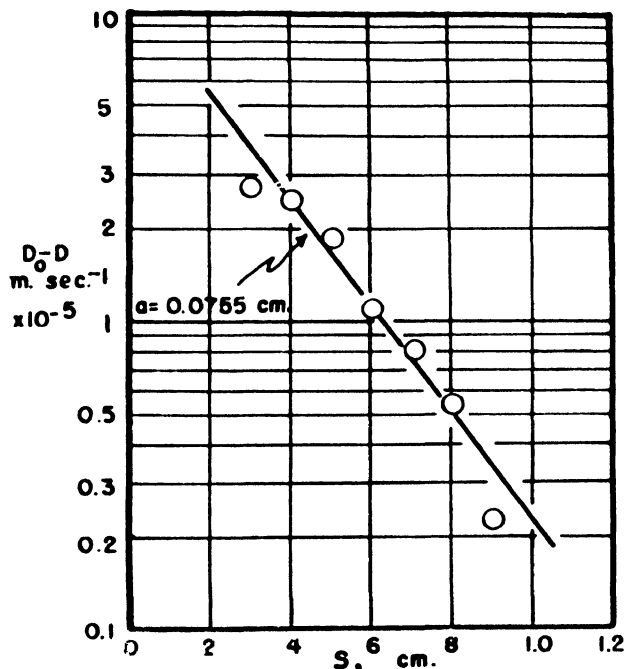
FIG. 34. Reaction zone curve for TNT. $V_0 = 1.0$ cm.^{3}g.$^{-1}$; $R = 1.27$ cm. Photograph No. 11, Explosives Research Laboratory, Bruceton, Pennsylvania.
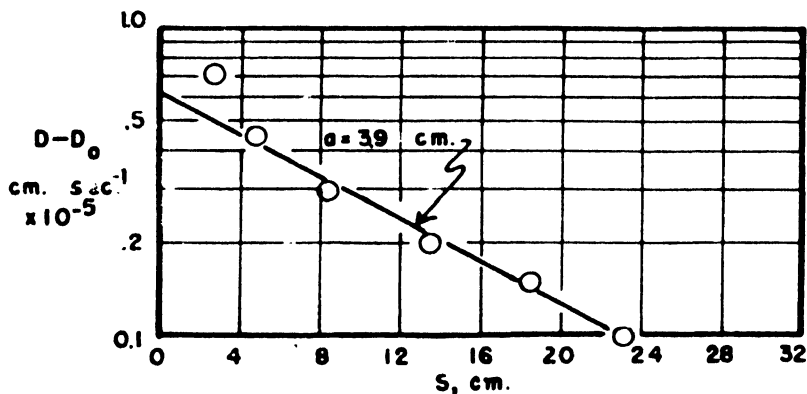
FIG. 35. Reaction zone curve for 80/20 Amatol. $V_0 = 0.61$ cm.^{3} g.$^{-1}$ Particle size: ammonium nitrate $\sim 10\ \mu$, TNT $\sim 70\ \mu$. Photograph No. 3737, Explosives Research Laboratory, Bruceton, Pennsylvania.

be read from the graph of figure 14, it is quite easy to follow by a step-by-step integration the behavior of the detonation velocity for any desired initial condition.

This calculation is presented in figure 36 for a spherical wave initiated (1) at its ideal velocity and (2) at a very low velocity (assuming, in the latter instance, that the reaction zone length remains constant so that failure does not occur).

Complications involved in the initiation process set difficulties in the way of the direct experimental study of transient spherical waves.

D. THE FAILURE OF DETONATION

The mere fact that a detonation wave has once been set up in an explosive charge is by no means a guarantee that the wave will continue to propagate. The wave may travel with a lower and lower velocity, until eventually it is moving so slowly that chemical decomposition is observed to cease and the wave subsequently travels as a sound wave. This behavior will be described as "failure of detonation." Under laboratory conditions, it is observed by the disappearance of the luminous trace on a high-speed photograph, by the lack of mechanical effect on a lead plate adjacent to the explosive, and by the recovery intact of the
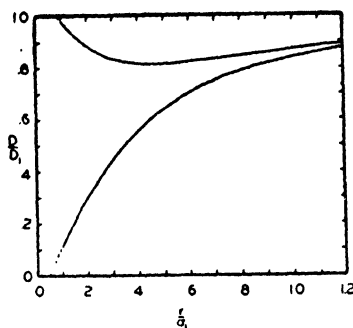
FIG. 36. Transient spherical waves

undetonated portion of the charge. Under conditions of service use, the failure phenomenon (also called "fading") in a high explosive leads to an only partial utilization of the chemical energy of the explosive, with a corresponding loss of mechanical effectiveness.

The discussion is here intentionally limited to the situation in which a detonation wave is once set up but subsequently fails. Specifically excluded is the more general problem in which the explosive is subjected to heating (either directly or by a mild blow) which initiates chemical decomposition, which then may or may not accelerate rapidly enough to build up a pressure shock leading to detonation. The greater physical complication of the process by which burning goes over into detonation adds tremendously to the mathematical difficulty of the problem. Some steps toward the solution of this more general initiation problem will be presented as a separate part of this paper.

In the program of experimental study of the sensitivity of military high explosives, a variety of measurements have been made of the conditions for failure of detonation. By combining the already developed theory of detonations with

lateral losses and the familiar theory of chemical reaction rates, we succeed in obtaining a theoretical criterion for failure. This theory permits a correlation of measurements already made and also suggests a direction for new measurements.

1. Theory of failure

In the theory developed in Section II B for the detonation velocity in a finite charge, it was supposed that the reaction zone length a remained constant. We shall now further assume that if we remove this restriction (thus let a depend upon D), the previous results remain applicable. Then the velocity in an uncased charge will be

$$\frac{D}{D_i} = 1 - 0.5 \frac{a}{R} \tag{38}$$

where a can now depend on D. This assumption will surely be justifiable if a is only a slowly varying function of D.

Next, we investigate the dependence of the reaction zone length on detonation velocity. The reaction zone length is proportional to the reaction time τ:

$$a = \frac{V_1}{V_0} D \cdot \tau \tag{34}$$

The reaction time τ is the reciprocal of a specific rate constant for the chemical reaction, and is therefore dependent upon the temperature according to the law (34):

$$\frac{1}{\tau} = \frac{kT}{h} e^{\Delta S^{\ddagger}/R_0} e^{-\Delta H^{\ddagger}/R_0 T} \tag{62}$$

where k = Boltzmann's constant, 1.38×10^{-16} erg deg.$^{-1}$

h = Planck's constant, 6.624×10^{-27} erg sec.

R_0 = the gas constant, 1.986 cal. deg.$^{-1}$ mole^{-1}

$\Delta S^{\ddagger}$ = the entropy of activation for the reaction, cal. deg.$^{-1}$ mole^{-1}, and

$\Delta H^{\ddagger}$ = the heat of activation for the reaction, cal. mole^{-1}.

The reaction zone will therefore become longer as the temperature in the reaction zone falls lower.

Now the temperature T where the reaction is occurring will be throughout the reaction zone substantially the same as T_1 at the end of the reaction zone (see figure 2 in Section I of this report). So long as the detonation wave is traveling at its ideal velocity, the temperature T_1 is a constant independent of the initial density (see equation I:6c).

In particular, this rules out the possibility of finding the dependence of reaction zone length on temperature by using explosive charges of various initial densities. (The reaction zone length does in fact have some dependence on initial density, but this is for an entirely different reason which will be discussed later.)

However, a detonation wave with radial losses was seen to be equivalent to an ideal wave with a smaller heat of reaction (see discussion in Section II B).

For such a wave, the temperature is proportional to the heat of reaction, while the square of the detonation velocity is proportional to the heat of reaction, so that the temperature depends on the velocity according to the relation:

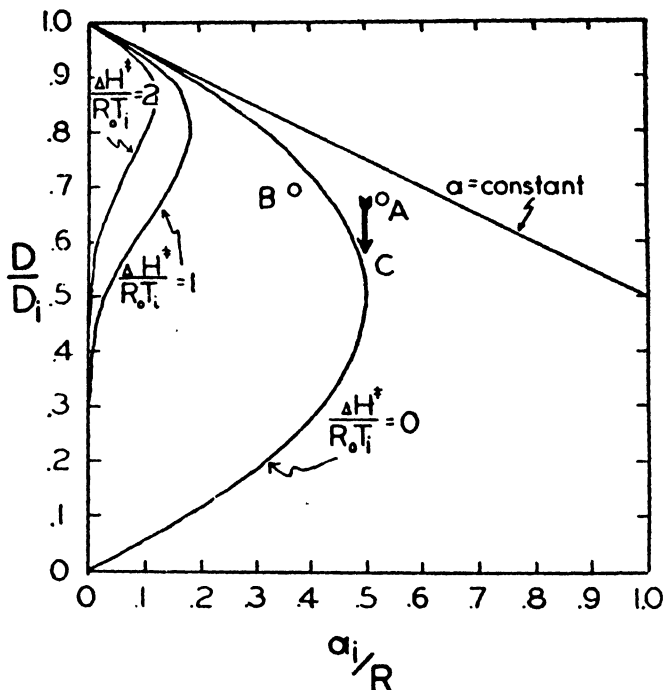$$\frac{T}{T_i} = \frac{D^2}{D_i^2} \tag{63}$$

Fig. 37. Failure chart

Upon combining equations 34, 62, and 63, one obtains the desired dependence of reaction zone length on detonation velocity:

$$\frac{a}{a_i} = \frac{D_i}{D} e^{\frac{\Delta H^{\ddagger}}{R_0 T_i}\left[\frac{D_i^2}{D^2}-1\right]} \tag{64}$$

Here a_i is the reaction zone length when the velocity is the ideal velocity D_i.

With the aid of equations 38 and 64, it is now possible to prepare a graph of D/D_i against a_i/R for any desired value of the heat of activation parameter $\Delta H^{\ddagger}/R_0 T_i$. This has been done in figure 37 for $\Delta H^{\ddagger}/R_0 T_i$ equal to 0, 1, and 2.

The final results of the failure theory, as presented in figure 37, are important enough to deserve some additional comment. In the first place, there exists a minimum radius of the explosive charge below which no stable detonation will propagate; at however high a velocity such a charge be initiated, it will build downward until it eventually fails. The critical radius (in units of the ideal reac-

tion zone length) and the corresponding critical velocity (in units of the ideal velocity) depend only on the heat of activation parameter. Conversely, if the critical radius and velocity can be measured experimentally, the heat of activation can be computed.

For any charge radius greater than the critical radius, there can be *two* steady velocities corresponding to the two branches of the curve. The upper velocity is the stable velocity commonly measured; any initially imposed velocity above this should build down to it, while one below should build up to it. The lower velocity is a metastable velocity; any initially imposed velocity slightly above should build on up to the high velocity, while any initial velocity below should build down to failure. A lower limit for the lower branch of the curve is, naturally, the velocity of sound in the intact explosive.

For solid explosives, there do not seem to be examples of measured velocities which can unequivocally be assigned to the low-velocity branch of the curve. Some workers believe that they have set up a "low-order detonation" in a solid; but usually the possibility has not been excluded that such waves are transients, or are exhibiting a time lag or a directional effect at the point of initiation. It is quite reasonable that the lower curve be observed *only* as the limit above which build-up occurs and below which failure occurs.

For liquid explosives such as nitroglycerin, nitroglycol, methyl nitrate, and the gelatin dynamites, it has repeatedly been observed that two steady velocities are possible—one in the neighborhood of 8000 m. per second, the other in the neighborhood of 2000 m. per second (Lawrence and others (2, 22, 26, 28, 31, 33)). It is most tempting to assign the low-velocity detonation to the lower branch of the curve of figure 5. In this case, it is necessary to assume that although the velocity is too low to build up, it is in some way prevented from failing completely —possibly by the small but regular amount of reaction occurring in especially sensitive regions such as bubbles in the liquid. The following observations (references cited above) on the low-velocity detonation in liquid explosives are consistent with the proposed explanation:

(*i*) The velocities are near sonic. Thus the low-order detonation velocity in nitroglycerin is about 2000 m. per second; the velocity of sound in liquid glycerol is 1960 m. per second.

(*ii*) The low-velocity detonations are always initiated by weak priming charges. The low-velocity detonation can sometimes go over into a high-velocity detonation (as by propagating into a larger tube), but a high-velocity never goes over into a low-order detonation.

(*iii*) The rate of chemical reaction is so small that a large part of the explosive remains unreacted after the passage of the wave. Thus the mechanical effect of the low-velocity wave is very small. Also, unreacted nitroglycerin can be detected among the detonation products. And most striking of all, enough unreacted material is left for a second low-velocity detonation wave sometimes to be initiated (perhaps at a particularly reactive spot) at a distance behind the first, and then to be propagated following the first . . . and occasionally in the opposite direction as well.

(*iv*) The low-velocity detonation travels at a *lower* velocity the larger the

radius of the charge. This is a notable observation, quite contrary to the usual observation on high-velocity detonations and difficult to explain on any hypothesis other than that here offered.

2. Application to experimental data

The determination of the critical minimum charge radius below which failure always occurs is not easy in practice, since it requires the preparation of a number of casting molds of various diameters. This has been carried out in a few instances by, e. g., Ubbelohde, Cybulski, and coworkers. The data are tabulated in table 9.

<div align="center">TABLE 9</div>

Cast TNT with 5 per cent Tetryl, density 1.6
Critical radius.	1.27 cm.
Reaction zone length.	0.668 cm. (see figure 20)
Critical velocity	4860 m.sec.$^{-1}$

Point A:
Ideal velocity.	7140 m.sec.$^{-1}$
a_i/R	0.525
D/D_i.	0.681

Cast 60/40 Amatol of density 1.5;
nitrate 92 cm.^{2}g.$^{-1}$
Critical radius.	1.588 cm.
Reaction zone length.	0.586 cm. (see figure 20)
Critical velocity	4800 m.sec.$^{-1}$

Point B:
Ideal velocity.	6920 m.sec.$^{-1}$
a_i/R.	0.37
D/D_i.	0.695

Clear cast TNT in conical charges.
Critical radius	1.0 cm. (see discussion in text)
Reaction zone length.	0.5 cm.

Point C:
Critical velocity.	?
a_i/R.	0.5

The experimental method of Tranter and Ubbelohde is interesting. They used conical test charges of TNT, initiated at the base of the cone, and noted the diameter at which failure occurred. Their results are given as a full-scale drawing in figure 38. They found that the failure diameter depended upon the cone angle, being smaller for a greater angle; this is to be expected, since in a cone of large angle, the transient wave has some additional stability because it has recently come from a region of large radius. The value of 1.0 cm. taken for clear TNT in table 9 has been extrapolated so as to compensate roughly for this cone effect.

The effect of particle size (clear vs. cloudy vs. creamed TNT) is easily visible in figure 38.

The critical diameters and velocities computed in table 9 are plotted in figure 37. It appears from these results that the appropriate value of the heat of activation is zero, or at most a few kilocalories. We shall return in Section II E to discussion of the implications of this numerical result.
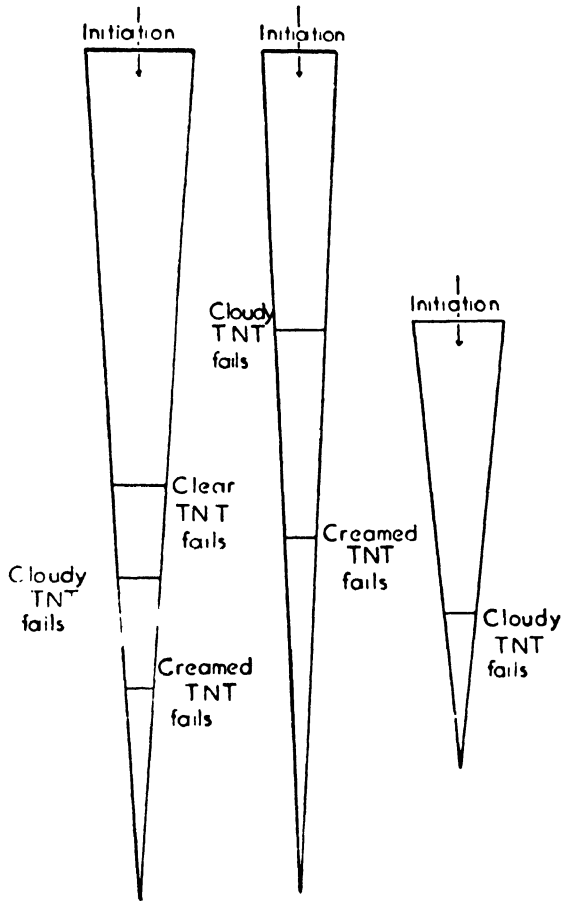
FIG. 38. Fading in conical charges

3. The failure diagram and the general measurement of sensitivity

The theory of failure as here developed rests upon two assumptions: of the effect of lateral loss on detonation velocity (equation 38), and of the effect of temperature on reaction rate (equation 64). While the particular shape and numerical values of the curves in figure 37 are decided by the particular forms and numerical parameters of equations 38 and 64, the existence and general shape of a curve similar to those in figure 37 are implied by the mere *existence* of the effect of lateral loss on detonation velocity and the effect of temperature on reaction rate. It is therefore legitimate to propose, independently of a particular

detailed theory, that a diagram like that of figure 37 could be prepared as a summary of the shock sensitivity of any explosive preparation. To prepare such a diagram, it would only be necessary for each of several charge diameters to run tests in which the samples had impressed on them shock waves of various velocities. Such a wave would be produced by hitting the sample with a calibrated shock wave.

The general principle of measuring sensitivity by means of a calibrated shock wave is by no means new; in fact, this is the guiding principle behind most of the familiar methods of testing sensitivity (exceptions being the drop test and the flame test). That this is so is evident when one lists the methods by which a calibrated shock wave can be set up.

(a) Gap tests

One method of controlling the intensity of a shock wave is to produce it with a standard "sender" charge, but then to allow it to attentuate over a controlled

TABLE 10

Data on gap test

Initiator, one No. 6 Electric Blasting Cap; gap, a number of sheets of paper of 0.080 mm. thickness; receiver charges, 5-g. pellets of 16 mm. diameter

EXPLOSIVE	MINIMUM NUMBER OF SHEETS PRODUCING AT LEAST ONE FAILURE	MAXIMUM NUMBER OF SHEETS FOR WHICH DETONATION OCCURRED
NENO, density 1.58–1.60	23	25
Tetryl, density 1.51	25	26
Tetryl, density 1.60	24	24
RDX-BWX 91-9, density 1.54..	14.5	15.5
RDX-BWX 91-9, density 1.50....	14	15
RDX-BWX 94-6, density 1.58....................	17	18.5
RDX-TNT 55-45, density 1.59....	17	19
TNT, density 1.52–1.56...	0	8–10 (?)

gap length of some inert material before striking the "receiver" or test sample charge. An air gap is commonly used (H. L. Porter), or a gap composed of layers of paper gives very good results (54); water gap tests find occasional use.

A minor disadvantage of the gap-test method is that in the present state of shock wave theory, and particularly with the matching problem introduced at the boundaries sender‖gap and gap‖receiver, it is difficult to obtain an absolute calibration. This difficulty might be obviated by photographic measurement of initial velocities in the receiver charges; or, for routine purposes, the gap distance itself may be used as a measure of sensitivity.

A definite advantage of the gap-test method is its high degree of reproducibility. For example, in the data by Herzberg and Walker listed in table 10, in which a gap of some twenty sheets of paper was used, with one (or at most two) more sheets of paper every shot failed; while with one (or at most two) less sheets of paper every shot went off. This excellent reproducibility of gap tests, which is to a great extent shared by the other shock wave tests, must be contrasted to the

poor reproducibility obtained in drop tests. In the latter, the statistical fluctuation in apparent sensitivity at a given height of fall is so pronounced that it is necessary to test many samples at each height, and then to report the sensitivity in terms of the height for which 50 per cent of the samples detonate.

(b) Minimum initiating charge tests

Another method of producing a shock wave of controlled intensity is to use an initiator charge of only finite size; then the rarefaction wave coming from the rear and the edges of the initiator charge will cut down the intensity of the shock wave set up in the test sample.

Of the sensitivity tests in which the amount of the initiating charge is varied, the simplest is the test for the standard size of electric blasting cap which will produce consistent detonation. Because of the limited number of sizes of such caps manufactured, this test is necessarily rough and not suitable for research purposes.

TABLE 11

Minimum priming charge test

Initiator, silver azide of density 2.98, amount as listed; receiver, explosive as listed

EXPLOSIVE	MINIMUM PRIMING CHARGE
	grams
Tetryl.	0.02
Picric acid...	0.035
TNT. ...	0.07
Trinitroxylene	0.25
Trinitroanisole .	0.26

An improved test of this sort is the minimum priming charge test, which measures the minimum amount of an initiating explosive needed to produce consistent detonation of the test samples. The minimum priming charge is widely used in practical testing of sensitivity. Table 11 gives a few representative results from the paper by Wohler and Martin (76). In minimum priming charge tests, typical initi o are metallic azides or fulminates. These are so effective that only a few centigrams of the initiator are needed. With such a small initiating charge, the shock wave in the receiver approximates a spherical wave.

A further improvement is the minimum boostering charge test, which measures the minimum length of booster (e.g., pressed Tetryl pellets) needed to produce consistent detonation of the test samples. The use of Tetryl (or a similar explosive) in place of azides or fulminates requires an initiator charge large enough so that the shock wave in the receiver is substantially a plane wave. Table 12 gives a few representative results from a report by Lawrence.

In all the types of minimum initiating charge tests, control over the intensity of the shock wave is achieved by causing a rarefaction wave to overtake the shock wave and to eat it away. Part of this rarefaction wave enters from the edges of the initiator, part from its rear: thus in the minimum boostering charge

experiments both the length and the diameter of the initiator charge must be taken into consideration.

Because the controlled shock wave is set up by a rarefaction superposed on a shock wave, the intensity of the shock wave in the test sample depends markedly on time and on distance. For so transient a wave, the theoretical solution of the hydrodynamic problem is almost prohibitively difficult and has not yet been carried through. The difficulty of the theoretical analysis is a serious disadvantage of all the minimum charge tests.

Since the test conditions in the minimum initiating charge tests resemble closely the conditions of actual use of explosives, the results of such tests can often be applied directly to full-scale design problems.

TABLE 12

Minimum boostering charge test

Initiator, pressed Tetryl pellet of density 1.56–1.60, diameter 1 in., length as listed; receiver, cast TNT, diameter 1¾ in., length 3½ in., cooled as listed

EXPLOSIVE	LENGTH OF BOOSTERING CHARGE	RESULTS
	inches	
TNT cooled in 40 min.....	¾	Five complete detonations
	½	One partial, one slight partial detonation
TNT cooled in 80–100 min..	1¼	Five complete detonations
	1	One complete, two partial detonations
	¾	One complete, one partial, one failure
	½	One failure
TNT cooled in 10 hr......	3*	Four complete, one partial detonation
	2½*	One partial detonation
	2*	Three complete, 1 partial detonation
	1½*	One complete, one partial detonation
	1*	One slight partial detonation

* Tetryl pellets of diameter 1½ in.

(c) Initiator composition tests

Yet another method of producing a shock wave of controlled intensity is to control the chemical composition of the initiator. By starting with a high-velocity explosive (e.g., RDX) and progressively reducing its heat of explosion per gram —suitably by addition of an inert compound of similar physical properties— an explosive with any desired detonation velocity can be prepared. With a graduated series of such explosives from which to choose initiator charges, a shock wave of any desired intensity can be set up in any receiver charge.

So far as the authors are aware, the idea of a series of standard initiator explosives for sensitivity testing has not heretofore been applied or even suggested. From the point of view of mathematical analysis of experimental results, such a testing method would have two particular advantages: (a) Since the density of

the initiator could be made the same as that of the receiver (or as close to it as desired), and since the initiator and test explosive would be in direct contact, no problem would arise of matching pressures and velocities at interfaces, of reflected shocks or reflected rarefactions. (b) Since the dimensions of the initiator charge could be increased without limit, all effects due to rarefaction waves at the sides or rear of the initiator could be wiped out. The same holds for any effects for which a finite reaction zone length in the initiator is responsible.

The proposed test method would therefore be free of the one serious fault of gap tests, and of the one serious fault of minimum initiating charge tests. It may prove to be a useful supplement to existing tests.

To some extent, the shock wave set up in a receiver charge can be controlled by controlling the loading density of the initiator charge or the receiver charge
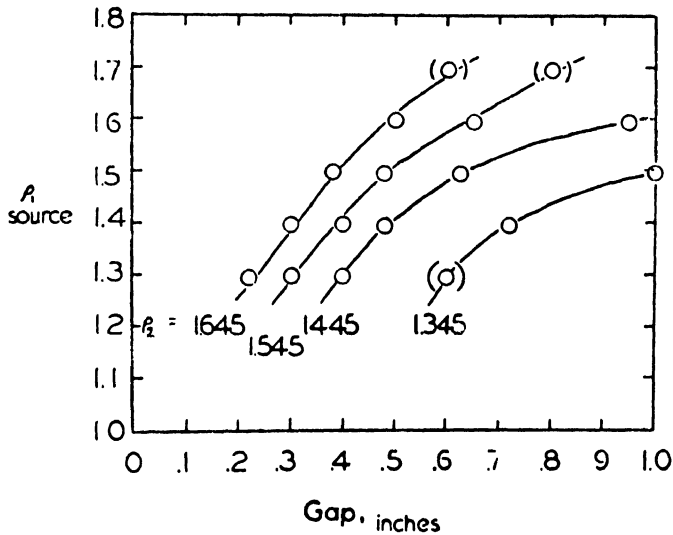
Fig. 39. Gap-test data (Porter)

To find exactly the behavior of a shock wave as it passes from a medium of one density into a medium of another density, it is necessary to match pressures and velocities at the boundary, and to take into account waves reflected from the boundary. A detailed discussion of this matching problem will be found in appendix F. For present qualitative purposes, it is enough to know that for a given initiator, a low-density receiver will experience a shock wave of higher velocity than a high-density receiver; also, for an initiator with a given heat of explosion, a high-density initiator will not only itself have a higher detonation velocity, but it will also set up shock waves of higher velocity than a low-density initiator. The direction and magnitude of these loading density effects is nicely illustrated by the experiment by Porter on Tetryl. Porter's data are plotted in figure 39, from which it can be seen that the more intense shock waves—longer gap jumped—are indeed found with high-density initiators and with low-density receivers.

The data by Porter do not lend themselves to quantitative mathematical analysis, because (a) the density variations were combined with a gap test, and (b) the Tetryl pellets were of such diameter that the ideal velocity was not reached, and of such length that not even the steady value was reached, as Porter has pointed out in his discussion of his results. In view of the serious radial losses and of the reflection phenomena at boundaries, a detailed theoretical analysis does not seem worthwhile.

The method of varying loading densities will always lead to reflected waves at the boundaries, and this detracts greatly from the value of the method as a tool for research. Moreover, the change of the density of the sample under test has some effect on the nature of its packing, which affects its reaction zone length; therefore, the density of the sample should not be changed if a study of reaction zone length is being made.

The effect of loading density on shock sensitivity, as illustrated in figure 39, is pronounced. It has repeatedly been observed under conditions of practical use that high-density explosives are much less sensitive than low-density explosives. For example, a gelatin dynamite which is detonated satisfactorily by a given cap at the earth's surface may fail when under the compression due to a few hundred feet of water. The same phenomenon is observable with some underwater bombs. We can now interpret all these density effects as due to the effect of density on the intensity of a shock wave entering the sample; and in any particular instance, we can solve the matching problem exactly to find the effect of density. On this interpretation, a low-density explosive is initiated by a shock while that same explosive at high density is not, for precisely the same reason that the low-density substance *air* is heated to incandescence by a shock wave from TNT while the high-density substance *steel* is heated a mere twenty degrees or so.

4. The failure distance

If an explosive charge is of radius less than a critical value, R_{crit}, it will surely fail no matter how strongly initiated. However, the failure does not take place at once; consequently the wave will travel some distance before the reaction ceases and it may be said to have failed.

The point of failure can be measured without difficulty on a moving-film or rotating-mirror photograph, or on a lead plate along which the explosive has been detonated. The distance traversed by the wave before failure has found some use as a routine measure of sensitivity.

A simple theory of the failure distance can be built upon the assumptions that the rate of building-down follows equation 57b, in which the steady velocity is given by equation 38 and the reaction zone length by equation 64.

$$a\,\frac{dD}{dx} = 0.333\,[D_s - D] \tag{57b}$$

$$\frac{D_s}{D_i} = 1 - 0.5\,\frac{a}{R} \tag{38}$$

$$\frac{a}{a_i} = \frac{D_i}{D}\,e^{\frac{\Delta H^{\ddagger}}{R_0 T_i}\left[\frac{D_i^2}{D^2}-1\right]} \tag{64}$$

The integration of this set of equations can be accomplished graphically, for any choice of $\Delta H^{\ddagger}/R_0 T_i$ and initial velocity. This, has been done for a heat of activation assumed to be zero (as indicated in figure 37) and initial velocity D_i, and the results are presented graphically in figure 40.

It will be seen from figure 40 that for a radius somewhat smaller than the critical radius, the distance traveled before failure is some tens of reaction zone lengths.

Inspection of the experimental results on 80/20 Amatol shows that, on the average, detonation in failures traveled about 8 cm. If this distance is twenty reaction zone lengths, then one reaction zone length is for 80/20 Amatol about 0.4 cm. Because of the highly approximate nature of this theory of failure distance, the numerical value computed for the reaction zone length must not be taken too seriously.
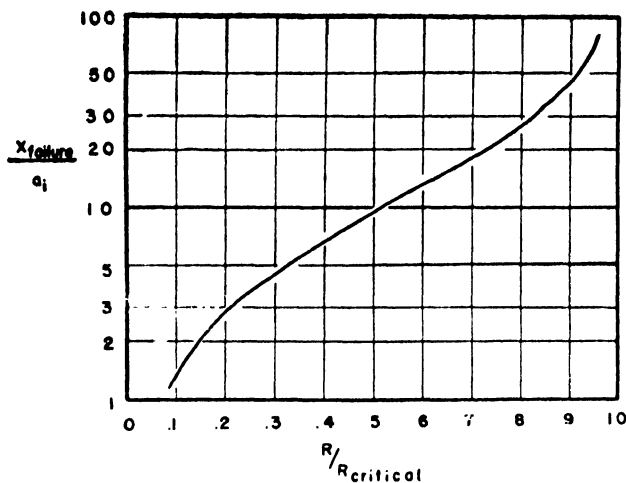
FIG. 40. Failure distance and charge radius for initiation at D_i, calculated for $\Delta H^{\ddagger}/R_0 T_i = 0$.

E. REACTION ZONE LENGTHS: SUMMARY

In the previous three sections (B, C, D) methods have been developed for computing the reaction zone length from experimental measurements on detonations in finite charges, on transient detonations, and on failure of detonations. We can now proceed to apply these methods to the available experimental data, in order to learn as much as possible about the chemical reaction in the reaction zone of a detonating explosive.

First we may point out the general result: *For typical high explosives, the reaction zone is about 1 mm. long.* The reaction zone ranges up to about ten times this length for the less sensitive explosives such as Amatol, and down to about one-tenth this length for the very sensitive explosives such as nitroglycerin.

The reaction zone lengths for the extremely sensitive primary explosives (azides, fulminates, DDNP, etc.) have not been determined. If, as seems likely,

their reaction zones are shorter than 0.1 mm., the experimental detection of any effects due to the finite reaction zone would be difficult.

It may also be pointed out that the three methods of computing reaction zone length, though they apply to different phenomena and are not essentially interdependent, agree in the numerical value which they assign to the reaction zone length. This circumstance gives us at least some degree of confidence in the results obtained.

1. The effect of grain radius

All solid explosives in actual use are composed of grains. These grains may range in size from a few microns upward to single crystals some centimeters across. The granular structure is sometimes produced intentionally by milling the explosive, but even cast explosives are granular polycrystalline materials, as may easily be seen under the microscope or inferred from the fact that the density of cast explosives is below the single-crystal density.

At first glance, it might be supposed that the granular nature of an explosive would be of no significance, that the high temperature in the detonation wave would first vaporize all the explosive, which would subsequently react according to the kinetic laws for homogeneous reactions. But this is not so. In the short time during which the explosive grain is exposed to the high temperature (a microsecond, more or less) the heat is unable to penetrate deeper than the surface layers. Consequently, each grain of explosive begins reacting at its hot surface, and the reaction progresses layer by layer until it reaches the center of the grain. The reaction for each grain within the reaction zone of a detonation is thus a sort of "cigarette burning," in which one layer of molecules is not ignited until the previous layer is consumed.

This *grain-burning theory* is supported by two kinds of arguments: the first from the impossibility of heat conduction through a grain, and the second from the experimentally observed effect of grain radius on the reaction time.

(a) Heat conduction into a grain

We wish to solve the following problem: If a cold spherical grain of substance (not reacting) is immersed in a heating bath, what is the temperature within the grain as a function of time and distance? Such a heating problem occurs frequently in engineering calculations, and graphs for its solution are available in several textbooks on heat flow or in engineer's handbooks (36). (This model is a reasonably good approximation to the actual problem of heat flow into a reacting sphere, for (*i*) the temperature outside a grain is substantially constant, and (*ii*) because of the endothermic nature of the first steps in a decomposition reaction, the chemical reaction at the immediate surface will not contribute to the heating in any important degree.) With the aid of these graphs, calculations have been made of the temperature distribution in a grain of 100 microns diameter, with an assumed thermal diffusivity $\kappa V/C_v$ of 0.018 cm.^{2} sec.$^{-1}$

The results (figure 41) show that even though the outside of a grain is at high temperature, the inside of the grain will remain cool for times of 1 microsec. or less. Chemical reaction must therefore proceed preferentially at the surface.

(b) Kinetics of a two-thirds-order reaction

If a sphere is ignited at its surface and reaction proceeds inward to the center, its rate law can be found as follows: The number of molecules reacting per second will be given by the product of the reaction rate for one molecule into the number of molecules on the surface:

$$\frac{dn}{dt} = k_r \frac{4\pi R^2}{s} \tag{65}$$

The number of molecules reacting per second will also be given as the time rate of change of the number of molecules in the sphere:

$$-\frac{dn}{dt} = \frac{d}{dt}\left[\frac{4/3\pi R^3}{v}\right] = \frac{4\pi R^2}{v}\frac{dR}{dt} \tag{66}$$
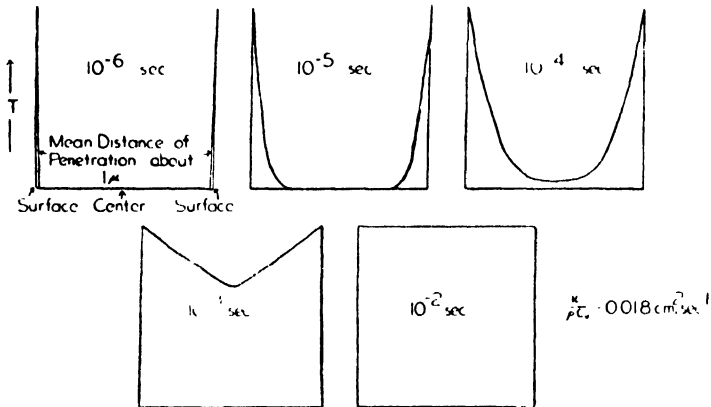
FIG. 41. Distribution of temperature in a sphere of diameter 100 μ, heated at the surface

Here n is the number of molecules unreacted; k_r is the specific reaction rate (reciprocal mean life) for one molecule, R is the grain radius at any time, s is the effective cross sectional area of one molecule, and v is the volume per molecule.

Upon combining equations 65 and 66, we obtain the desired rate law for the grain-burning reaction:

$$\frac{dR}{dt} = k_r \frac{v}{s} \tag{67}$$

Thus the grain will burn at a rate which is radially constant. The ratio v/s is approximately the diameter λ of a molecule and will be so written. Then for every molecule reacting, the radius decreases by one molecular diameter. However, it must be pointed out that s is the *effective* cross-sectional area of a molecule and to the extent that a molecule fails to "shade" the molecule below it, heating can occur into more than the top layer; the effective area of a molecule will then be smaller and the ratio v/s larger than one molecular diameter.

The time τ required for complete reaction is merely the time required for the reaction to traverse the grain radius R_g:

$$\tau = \frac{1}{k_r} \frac{R_g}{\lambda} \tag{68}$$

Since the extent of reaction $N = 1 - (R/R_g)^3$, the rate law (equation 67) for grain-burning becomes:

$$\frac{dN}{dt} = \frac{3k_r\lambda}{R_g} (1 - N)^{2/3} \tag{69}$$
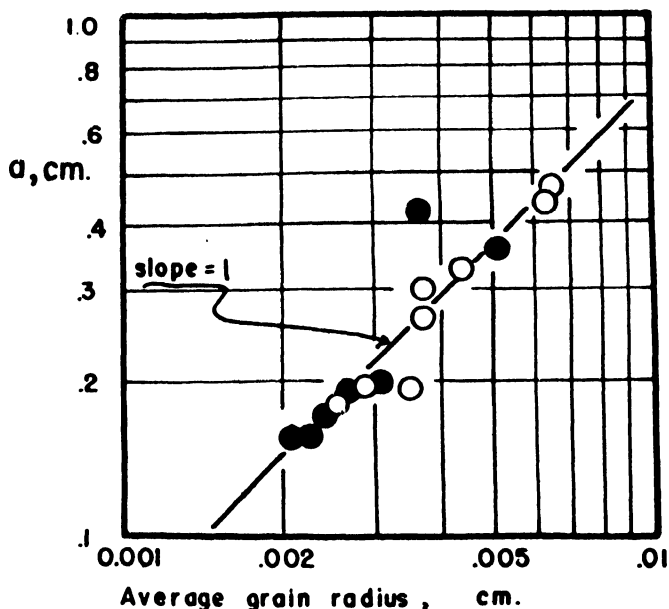
FIG. 42A. Reaction zone length and grain radius: O, 60/40 Amatol; ●, 50/50 Amatol; □, ammonium picrate, $V_0 = 1.0$; △, TNT, $V_0 = 1.0$.

and the reaction is of two-thirds order. (For the integrated form of the two-thirds-order rate law, see appendix G.)

According to equation 68, if an explosive is undergoing grain-burning, its reaction time τ should be proportional to its grain diameter.

As a test of the grain-burning theory, we may now graph the reaction zone length (as determined by the theory of Section II B) as a function of grain radius. This has been done[19] in figures 42A and 42B for the available data (D. P. Mac-Dougall et al.) in which grain size was varied, for 60/40 and 50/50 Amatols, for

[19] In the analysis of these data the average grain radii were computed from the surface areas given by the authors. The ideal detonation velocity was taken to be 6500 m.sec.$^{-1}$ for 50/50 Amatol and 6150 m.sec.$^{-1}$ for 60/40 Amatol.

ammonium picrate[20] of density 1.0, and for TNT[21] of density 1.0. The data plotted in figure 42, particularly those for Amatol and ammonium picrate, fall nicely along a straight line of slope unity on logarithmic paper. This is confirmation of the grain-burning law for these particular explosives, and there is no reason to suppose that the grain-burning phenomenon is other than a general phenomenon to be observed in every solid explosive.

In view of the key role played by reaction zone length in the stability of propagation of detonation, the conclusion that solid explosives undergo grain-burning makes it a matter of first importance to know and to control the grain size of explosives. Thus a fine-grained explosive should always detonate stably, while in
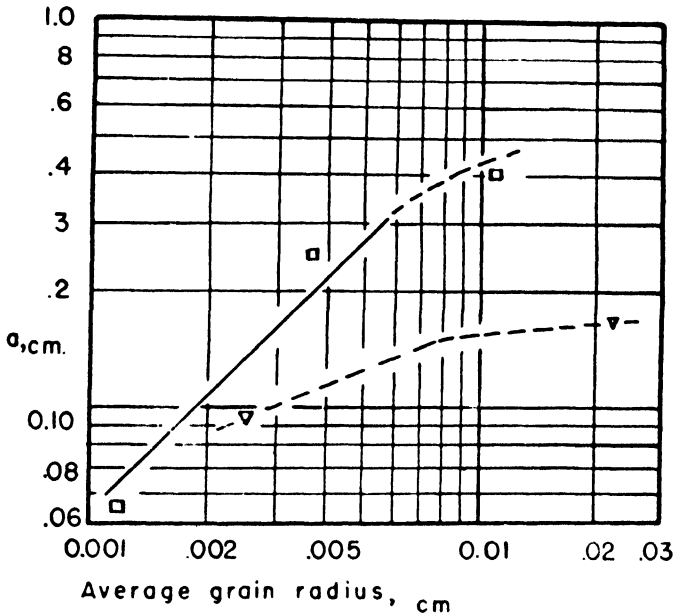
FIG. 42B. Reaction zone length and grain radius

a sufficiently coarse-grained explosive (say a large single crystal) it might well be impossible to maintain a stable detonation wave.

In some of the older measurements of shock sensitivity and of velocities in finite charges, the grain size was not known or controlled. Such measurements are not of much value. In recent investigations, the importance of grain size has been realized, and the observation has repeatedly been confirmed that coarse-grained explosives can only with difficulty be made to detonate. We may cite the experiments by Lawrence and by Woodhead and Wilson, already mentioned in this report in table 12 and figure 36, respectively.

Lawrence found that TNT cooled in 45 min. gave crystals of average size 50 x 50 x 500 microns: TNT cooled in 75 min. gave crystals of average size

[20] See figure 20 of this paper.
[21] See figure 23 of this paper.

100 x 100 x 700 microns; while with TNT cooled in 10 hr. very large crystals were obtained, some running the entire length of the charge (3.5 in.). With the normally cooled TNT, a 15-g. pellet of Tetryl was sufficient to produce five complete detonations; with the slowly cooled TNT, a 26-g. pellet of Tetryl was required to produce five consecutive shots; while with the very slowly cooled TNT, even 144 g. of Tetryl produced only four complete shots and one partial shot. "This illustrates the known fact that TNT cast clear (90°C.) and allowed to cool slowly is very insensitive."

Woodhead and Wilson found in their dying-out experiments using conical charges that cast TNT poured clear (large crystals) was considerably less sensitive than the poured cloudy (smaller crystals), which in turn was less sensitive than the same TNT creamed (still smaller crystals).

Tranter and Ubbelohde found that the addition of a eutectic proportion of such substances as RDX, PETN, hexanitrodiphenylamine, or dinitrobenzene produced TNT crystals which were markedly smaller. In such an explosive, "fading" in sticks of 1 in. diameter was completely or partly suppressed. Tranter and Ubbelohde also mention that "sensitization of cast TNT in shells, by creaming, improves fragmentation to about the same extent as the addition of 30% Tetryl."

Copp and Ubbelohde also note that "the addition of aluminum to 50/50 Amatol, to form Minol 2, has a marked effect in reducing the average cross-section of the TNT crystals in the casting."

With very large grains, there is some question as to what to take for the "grain size," for there is sure to be ignition at some of the crystal interfaces within the grain. Presumably this is the explanation for the behavior of TNT noted in figure 42B, in which a tenfold increase in grain size only gave a twofold increase in reaction zone length. Here the large grains were almost 0.5 mm. across, and apparently the explosive was polycrystalline with individual crystals smaller than this.

Liquid explosives propagate detonation in a manner not qualitatively different from solid explosives. They are initiated by shocks of about the same intensity as solids, and respond like solids to the effect of lack of confinement. Fragmentary data (34, 45, 55, 66, 70) suggest that liquids are if anything more sensitive than solids to initiation by shock, and that liquids have a reaction zone rather shorter than that of solids. Since a liquid is not composed of grains, another mechanism of initiation of liquid explosives must be found.

One may consider the following hypothesis for the initiation of liquid explosives: The decomposition of a liquid explosive is initiated at gas bubbles within the liquid. The detonation wave raises each bubble by compression to a temperature high enough to start decomposition, the temperature subsequently being maintained by the heat of decomposition. Reaction proceeds radially outward from each bubble. On this *bubble theory* the bubbles in liquids would play the same role as "hot spots" that hot grain surfaces play in solids. In fact, the linear rate of the surface reaction is the same whether reaction is proceeding inward toward or outward from a center. The time for complete reaction is just the time for the reaction to traverse half the interbubble distance. It does, therefore, have

some meaning to speak of a "grain" of liquid according t , the bubble theory, where we mean by a "grain" that aliquot part of the liquid surrounding each bubble.

The bubble theory is susceptible to direct experimental investigation: Bubbles might be removed from a liquid explosive by protracted vacuum treatment, or forced to dissolve completely by high hydrostatic pressure. Or, additional bubbles might be introduced into a liquid explosive by mechanical or chemical means. In the first instance, the liquid explosive should become less sensitive to shock, in the second instance, more sensitive (34, 45, 55, 66, 70). The solution to this problem must wait upon further experimental evidence. There is some circumstantial evidence for the bubble theory:

(*i*) It is well known that ordinary liquids do contain a considerable number of "bubble nuclei" (small bubbles) entrapped, and that those small bubbles can only with difficulty be removed. For the organic nitrates which comprise most liquid explosives, bubbles would continually be produced by the slow room-temperature decomposition of the explosive.

(*ii*) Whenever a shock wave traverses a liquid containing bubbles, the mere fact that the bubbles are gaseous (i.e., of low density) guarantees that they will become far hotter than the main liquid. (It will be recalled that the air adjacent to TNT is heated to incandescence.) Such hot regions would be the logical site for reaction to begin.

(*iii*) Bubbles in the liquid would provide just the sort of specially sensitive regions needed to explain why the low-velocity detonation does not fail completely (see discussion in Section II E). The region around each bubble may be supposed to react to a small extent—not enough to lead to complete reaction of its own "grain," but barely enough to initiate the next bubble.

2. The mean lifetime of an explosive molecule

The time required for the completion of reaction in a detonation, the reaction time τ, we have seen to be about a microsecond. But this time is not itself the reciprocal of the rate of any *elementary* reaction, and so to consider it is fallacious. It is rather the time required to complete a sequence of elementary reactions—namely, the reaction of one molecule after another, from the surface of a grain to its center.

With the aid of the grain-burning equation

$$\tau = \frac{1}{k_r} \frac{R_g}{\lambda}$$ (68)

and data such as those in figure 42, we can compute the true specific reaction rate k_r for a single molecule. The reciprocal of k_r is the true mean lifetime of a single molecule at the detonation temperature.

The specific reaction rates computed for the explosives of figure 42 are listed in table 13. Here the effective molecular diameter was assumed to be 10^{-8} cm. Since the frequency factor kT/h in the absolute rate law

$$k_r = \frac{kT}{h} e^{-\Delta F^{\ddagger}/R_0 T}$$

is at 3000°K. equal to 60×10^{12} sec.$^{-1}$, it is clear that the decomposition of a single explosive molecule is proceeding at a rate which is quite normal for an ordinary chemical reaction at that temperature. Only a moderate factor of 1/250 remains to be explained, and such a factor has a variety of possible explanations.

The knowledge that the reaction proceeds at a "normal" rate is not so decisive as might be supposed, toward the elucidation of the nature of the rate-determining reaction. Among the possible rate-determining reactions are the following: (*i*) Simple unimolecular decomposition, with a small heat and/or entropy of activation against it. (*ii*) Bi- or multimolecular reaction, the extra reactants being present at moderately high concentration in the hot gases (this would be "pseudo-unimolecular"). No restriction as to the number of reactants, nor their nature (ions, free radicals, etc.). (*iii*) Diffusion of reactants to, or products away from, the site of reaction. Diffusion of heat may also be the slow step.

3. Heat of activation of the decomposition reaction

The only present analysis which yields direct information on the activation energy of the reaction in the detonating explosive is the analysis of detonation

TABLE 13

Specific reaction rates for explosives of figure 42

EXPLOSIVE	REACTION RATE, k_r
	sec^{-1}
Amatol	0.2×10^{12}
TNT	0.3×10^{12}
Ammonium picrate	0.2×10^{12}

failure presented in Section II D. According to the result there found, the activation energy is zero or near zero—say within a half-dozen kilocalories.

This result is admittedly susceptible to further experimental testing. It is however not unreasonable, and if true is most suggestive.

Since the unimolecular decomposition would be expected to have a high activation energy, it would be ruled out. In any event, unimolecular decomposition as a rate-determining step does not seem particularly attractive from a chemical point of view; bimolecular (or multimolecular) reaction of free-radical (or ion) fragments with intact molecules seems more likely.

The same objection is to some extent applicable to bimolecular reactions, though here the case must be put less strongly, for free-radical reactions do sometimes occur with low activation energies.

Diffusion as a rate-controlling step is quite possible kinetically: If a reactant must diffuse to the site of the reaction, the specific rate k_d of its arrival at that site is

$$k_d = n_1 \frac{\lambda^2}{\Lambda^2} \frac{kT}{h} e^{-\Delta F^{\ddagger}/R_0 T} \tag{70}$$

where n_1 is the mole-fraction of such molecules in the solution, λ is the molecular diameter, Λ is the distance the diffusing molecule must traverse, and other symbols have their usual meaning. Since the activation energy for diffusion in condensed systems is only a few kilocalories, diffusion as a slow step would satisfy this requirement. Furthermore, if the concentration n_1 of diffusion reactants were not too large, or if the diffusing distance Λ were several interatomic distances, the absolute rate of the reaction would satisfy that requirement. It is perfectly plausible that at the high temperature involved, chemical reactions have become so fast that diffusion is the rate-determining step.

Another possibility is that the slow step is the diffusion of heat to the site of reaction. The rate of diffusion of heat obeys the same laws as the rate of diffusion of matter, except that the coefficients of diffusivity are somewhat different for the two processes:

$$\text{Diffusivity of matter} = \frac{kT}{h} e^{-\Delta F^{\ddagger}/R_0 T} \tag{53}$$

$$\text{Diffusivity of heat} = \lambda C_1 \tag{54}$$

For the reasonable numerical values of 3000°K. for temperature, 10^{-1} cm. for interatomic distance, 2×10^5 cm. sec.$^{-1}$ for the velocity of sound C_1, and zero activation energy for diffusion, those diffusivities become:

$$\text{Diffusivity of matter} = 0.60 \text{ cm.}^2 \text{ sec.}^{-1}$$
$$\text{Diffusivity of heat} = 0.02 \text{ cm.}^2 \text{ sec.}^{-1}$$

It is seen that the diffusivity of heat is the same as that of matter, to a factor of about 1/30. Therefore, the diffusion of heat would give even better numerical agreement with the absolute rate k_r found above than would the diffusion of matter. The two diffusion processes are alike in their slight dependence on temperature.

Remark concerning extrapolation of low-temperature measurements

It might be supposed that the heat of activation of the reaction in a detonation, as well as the specific rate itself, could be obtained by extrapolating to the detonation temperature measurements of the decomposition rate at room temperature or a few hundred degrees above. A considerable number of such measurements are available (1, 20, 30, 32, 33, 37, 48, 62, 63). In general, the rates measured upon heating at these low temperatures yield activation energies in the range 30–50 kilocal., and frequency factors in the range 10^{10}–10^{20} sec.$^{-1}$

Two remarks must be made concerning the extrapolation of those low-temperature data. The first remark is that even if the measurements are precise, any extrapolation of experimental data over an uncharted region four times as extensive as the region investigated, is of doubtful validity. As figure 43 shows, this is precisely the kind of extrapolation necessary to obtain reaction rates at detonation temperatures from reaction rates actually measured.

The second remark is that in different temperature regions, quite different re-

actions may be rate-controlling. In a sequence of consecutive reactions, the slowest reaction will always be rate-determining.

The full rate law for a sequence of reactions is, if a steady state is established:

$$\frac{1}{k_r} = \frac{1}{k_1} + \frac{1}{k_2} + \cdots \tag{73}$$

If two consecutive reactions have different activation energies, the reaction with higher activation energy will be rate-determining at low temperatures, and the reaction with lower activation energy will become rate-determining at high tem-
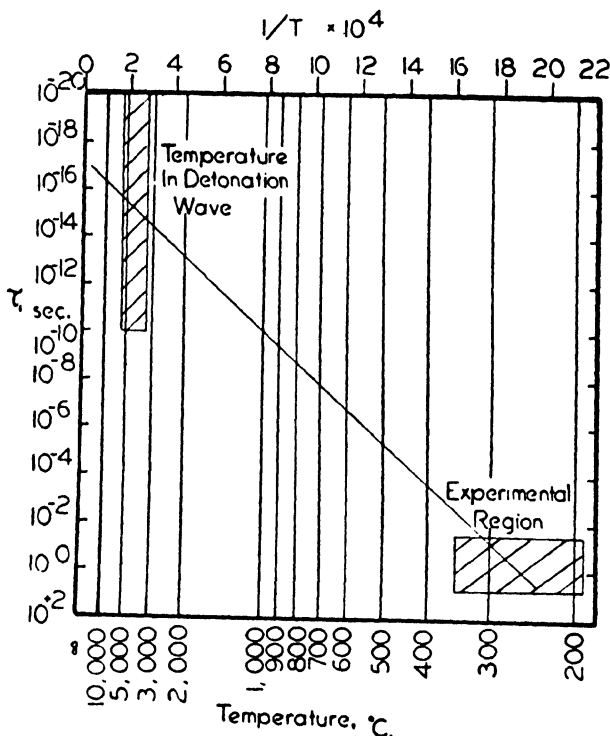
FIG. 43. Extrapolation of reaction time to detonation temperatures

peratures. It is evident that in the absence of a detailed knowledge of the reaction mechanism, one has no assurance that a complex reaction will even continue to be controlled by the same slow step as temperature is varied.

An interesting example of this phenomenon of change from one rate-controlling step to another in a set of consecutive reactions was found by Audubert (4) in the decomposition of metallic azides. Figure 44 gives his observations on the decomposition of sodium azide.

In view of these remarks, the extrapolation of low-temperature rate data to high temperatures does not appear to be acceptable.

4. The effect of packing

In an explosive composed of grains, the regions brought to the highest temperature upon impact of a shock wave will be the points of contact of grains. Such points are subject both to the greatest compressional heating and to greatest frictional heating. At such hot spots the chemical reaction will undoubtedly begin.
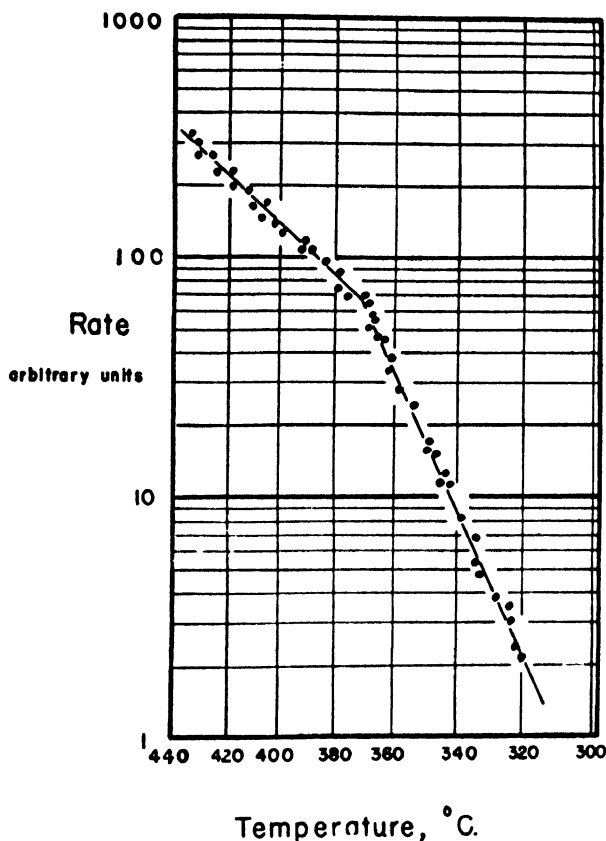
FIG. 44. Audubert's data on decomposition of sodium azide

So long as several such hot spots are present at the surface of each grain of explosive, the longest distance traversed by the decomposition will be the grain radius. The reaction zone length will then be substantially independent of the nature of the packing.

If, however, the number of load-bearing contact points is reduced to two, or one, or less than one per grain of explosive, the distance traversed by the decomposition will be much more than one grain radius. Under those conditions, the reaction zone length will be greatly increased, and the explosive will be correspondingly prone to fail. The reduction of the number of load-bearing contact

points can be accomplished in two ways: (*1*) the density can be decreased; (*2*) a mixture of small with large grains may be used. Both of these experiments have been tried on explosives.

(*1*) *Effect of low density:* In the close packing of spheres 74.5 per cent of the space is filled; in the simple cubic packing of spheres, 52.36 per cent of the space is filled (17, 18, 22). If, therefore, we take a typical high explosive of crystal density 1.65, each grain will not have twelve contact points below a density of about 1.2, and it will not have eight contact points below a density of about 0.9. The exact numerical values will depend on the shape of the crystals. Thus we
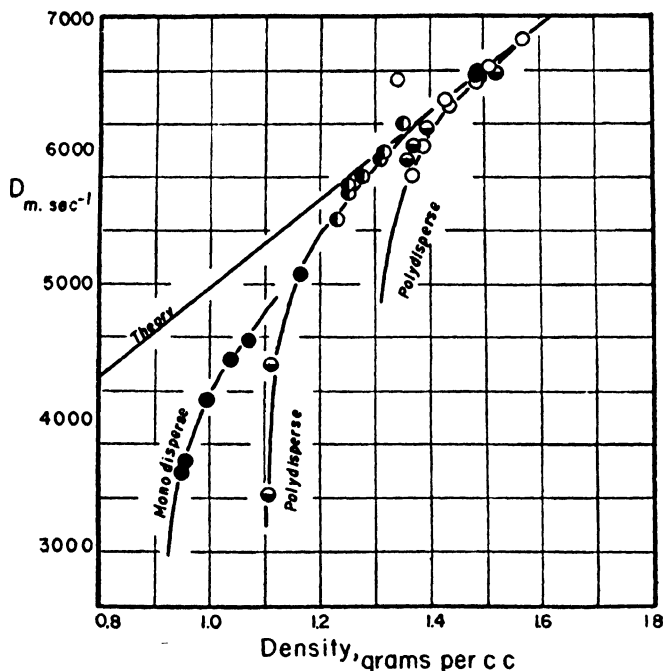
FIG. 45. Failure in Amatol due to mixed grain sizes. O, 200 μ ball-milled; ●, 177–250 μ; ◐ 70 μ; ◒, 30 μ.

might expect a perceptible lengthening of the reaction zone below density 1.2, and a marked lengthening below density 0.9. If the ratio of reaction zone length to charge radius is such that the effect on detonation stability is significant, any lengthening of the reaction zone will be fatal to the detonation wave.

Precisely this effect has been obtained by D. P. MacDougall and coworkers with ammonium picrate. The observed velocities for various densities are plotted in figure 45. It will be seen from figure 45 that below a certain density (which varies somewhat from preparation to preparation) the detonation velocity falls violently, and then detonation fails completely.

(*2*) *Effect of mixed grain sizes:* Suppose that a large number of spheres, all of the same diameter, be packed so as to have a particular percentage of voids.

Then the number of load-bearing contact points per grain will be independent of the actual diameter of the spheres: thus for 25.95 per cent voids the number of load-bearing contact points is twelve per sphere; for 47.65 per cent voids, the number of load-bearing contact points is six per sphere.

If now a collection of large spheres be packed so as to have any particular number of contact points per sphere, then small spheres can be put into the voids between the large spheres without changing the number of load-bearing contact points; for the small spheres can be so loosely packed as to bear little or no load. If the mixture of small and large spheres be then expanded to its original over-all density, the number of load-bearing contact points per sphere will have been decreased.

The more efficiently the small spheres pack into the voids of the large, the more effective will be the decrease in load-bearing contact points at constant over-all density. The efficiency of packing depends upon the per cent of large
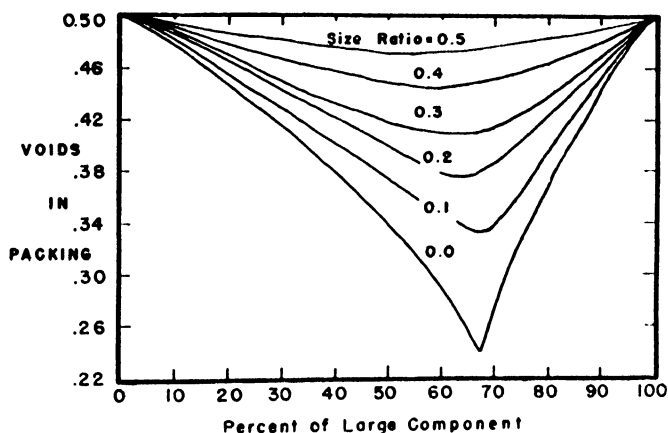
Fig. 46. Relation between voids and size composition in two-component systems of broken solids when the voids of single components are 0.5.

component in the mixture, and upon the size ratio of the spheres. This problem has been investigated by Furnas. As figure 46 shows, the packing is most efficient at about 65–70 per cent of the large component (31). Gamow has also shown by measurement of the electrical conductivity of packed ball-bearings of mixed sizes, that the number of load-bearing contact points (therefore conductivity) is a minimum at about 70 per cent of large ball-bearings.

It is now clear that if we mix explosive grains of two different sizes, the mixture will have many less load-bearing contact points than either of the mono-disperse explosive preparations from which it has been prepared. The effect would be most pronounced at a composition of about 70 per cent large grains. If the reaction zone length is such that the effect on detonation stability is significant, then the lengthening of reaction zone produced by such mixing will be fatal to the detonation wave.

Precisely this effect has been obtained with ammonium picrate of densities 1.0

and 0.95, using fine grains of less than 44 μ diameter, and large grains of 177–250 μ diameter. Figure 47 shows the striking decrease in stability of detonation caused by mixing small grains with large grains.

It should be possible roughly to estimate the effect of packing by a simple counting of the average number of load-bearing contact points per grain, as determined by the geometry of the packing. In any such counting, grains which are separated in the direction of propagation of the wave by a narrow gap (say 1/20 their own diameter) should be counted as being in contact, for they will be brought into contact by the mass movement behind the detonation front.
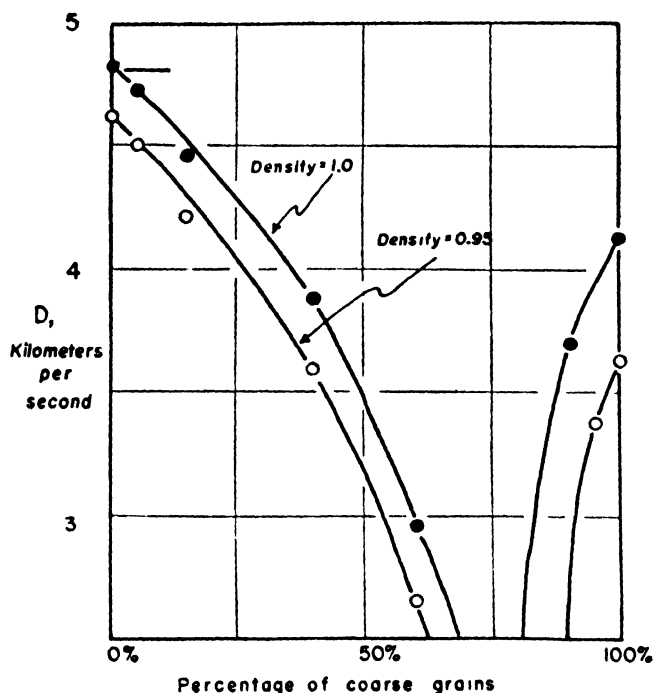
FIG. 47. Failure in D salt (ammonium picrate) due to mixed grain sizes

APPENDIX F. THE SHOCK WAVE AT MATERIAL BOUNDARIES

We wish to find the behavior of a shock wave as it crosses a boundary from one material into another. The general method of mathematical treatment of such a problem is well known (17, 18, 22). A shock wave will be sent into the second material, while a shock or a rarefaction wave will be reflected back into the first material, depending on whether the first material is less dense or more dense than the second. The amplitude of each of these waves is readily found by making use of the condition that the pressure P and the fluid velocity W must match at the boundary, together with the known P,W relations for shocks and for rarefactions.

The actual computation can of course be carried out numerically. An alterna-

tive method of great simplicity is to plot on a P,W diagram (*1*) the curve representing all possible shocks in the second material, and (*2*) the curve representing all possible reflection rarefactions (or shocks) in the first material; the crossing point of the two curves gives the desired matching conditions.

1. *P,W relation in a shock*

All the required relations for shock waves and detonation waves have already been derived in Section I of this report. From equations I:4d and I:6e, the relation between P and W is for a detonation wave:

$$\frac{P - P_0}{(W - W_0)^2} = \frac{\gamma + 1}{V_0 - \alpha} \tag{F1}$$

For a pure shock wave the relation between P and W is slightly different, being

$$\frac{P - P_0}{(W - W_0)^2} = \frac{1}{2}\frac{\gamma + 1}{V_0 - \alpha} \tag{F2}$$

Equation F1 or F2 permits us to plot the P,W relation for any intense shock or detonation wave. Here it has been assumed that the Abel equation of state holds, but an analogous equation is readily found for any desired equation of state.

For shock waves of low intensity (near sonic), it is more convenient to evaluate the P,W relation from equation 4e, which reads:

$$(P - P_0)V_0 = (W - W_0)D \tag{F3}$$

For near sonic velocities this becomes

$$\frac{P - P_0}{W - W_0} = \frac{C}{V_0} \tag{F4}$$

These equations (F1 or F2, and F4) are to be used for both the transmitted and the reflected shock wave.

2. *P,W relation in a rarefaction*

The following is a very simple derivation of the relations which hold in a rarefaction wave· It will be assumed that a steady state exists, so the equation of continuity is

$$\frac{dW}{D - W} = -\frac{dV}{V} \tag{F5}$$

The velocity of a rarefaction wave is equal to the local velocity of sound,

$$D = C + W \tag{F6}$$

where the velocity of sound is as usual defined by the relations for the Abel equation of state

$$C = V\sqrt{-\gamma\left(\frac{\partial P}{\partial V}\right)_\tau} \tag{F7}$$

and

$$C = V \sqrt{\frac{\gamma P}{V - \alpha}} \qquad C_0 = V_0 \sqrt{\frac{\gamma P_0}{V_0 - \alpha}} \qquad \text{(F7a, b)}$$

The expansion is assumed to be adiabatic (i.e., isentropic) so that for the Abel equation of state

$$P(V - \alpha)^\gamma = P_0(V_0 - \alpha)^\gamma \qquad \text{(F8)}$$

If equations F5 and F6 are combined, they give

$$W - W_0 = \int_V^{V_0} \frac{C}{V} \, dV \qquad \text{(F9)}$$

which is the basic equation for a rarefaction wave. This may be integrated when the appropriate value of C is inserted: with the value of C given by equation F7 with equation F6, this becomes

$$W - W_0 = \frac{2C_p}{\gamma - 1} \frac{V_0 - \alpha}{V_0} \left[1 - \left(\frac{P}{P_0} \right)^{(\gamma-1)/2\gamma} \right] \qquad \text{(F10)}$$

Equation F10 permits us to plot the P,W relation for any rarefaction wave in a substance obeying the Abel equation of state.

When the pressure and velocity have been found by the intersection of the two lines on the P,W plane, the shock velocity D can be obtained at once by the relation:

$$(P - P_0)V_0 = (W - W_0)D \qquad \text{(F11)}$$

The actual details of the matching technique can be illustrated most easily by a few worked-out examples:

Example: Shock wave produced in air by a normally incident detonation wave in TNT

Figure 48 gives the curves for a rarefaction wave sent into the detonation products of TNT and for a shock wave sent into air. Their intersection gives the pressure and velocity of the initial wave sent from TNT into air.

The rarefaction curve was computed according to equation F10 with

$$P_0 = 109{,}000 \text{ atm.}$$
$$W_0 = 1.02 \text{ km. sec.}^{-1}$$
$$C_0 = 5.83 \text{ km. sec.}^{-1}$$
$$\gamma = 1.24$$
$$V_0 = 0.540 \text{ cm.}^3 \text{ g.}^{-1}$$
$$\alpha = 0.4225 \text{ cm.}^3 \text{ g.}^{-1}$$

The shock curve was computed according to equation F2 with $\gamma = 1.4$, $V_0 = 0.845$ cm.^{3} g.$^{-1}$, and $P_0 = 0$.

The pressure and velocity of the air shock given by figure 48 are 2500 atm. and 52 km. sec.$^{-1}$, respectively. Those values are far higher than the values observed experimentally (about 600 atm. and 7.65 km. sec.$^{-1}$). This is partly the

fault of too simple an equation of state for air, but primarily the fault of using the Abel equation of state for the adiabatic expansion of TNT. Over such a large pressure range as here covered, the use of the Abel adiabatic introduces a large error. Investigations by Boggs and coworkers, G. I. Taylor, H. Jones, Strickland, Dasgupta, and Penney, in which the primary aim was the determination of accurate numerical values in these shock problems have used more elaborate equations of state, and have succeeded in obtaining excellent agreement between theory and experiment.
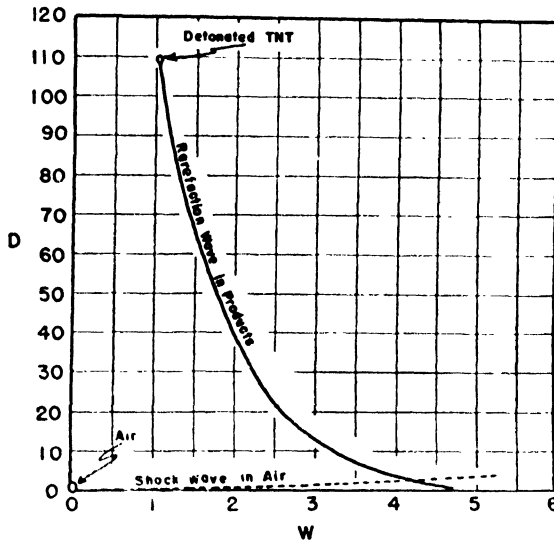
Fig. 48. P,W plot; TNT matched to air

Example: Reflected shock produced by a detonation
wave in TNT normally incident to a rigid wall

Figure 49 gives the curve for a shock wave sent into the detonation products of TNT, and the curve for a rigid wall. Their intersection gives the shock pressure produced when a detonation wave in TNT meets a wall.

The shock wave in the TNT products was computed according to equation F2 with the same numerical parameters needed for the previous example.

The P,W relation in the wall is very simple: The velocity of the wall is zero for any pressure.

At the intersection of the two curves, the pressure is 165,000 atm. It is interesting to point out that while a pure shock wave reflected at a wall always more than doubles its pressure, the same cannot be said for a detonation. This is because the P,W relations F1 and F2 are different for a shock and a detonation.

Example: Shock wave set up by a moving projectile

If the wall is moving rather than fixed, it is only necessary to displace the vertical line of figure 49 to the appropriate velocity. This has been done sche-

matically in figure 50, which represents the shock set up in a medium by a moving wall. Essentially this matching method was used by Taylor and Maccoll (67) to find the pressure at a moving wedge.

The equation of the shock curve in figure 50 is equation F1 or F2, depending on the magnitude of the velocity of the wall.
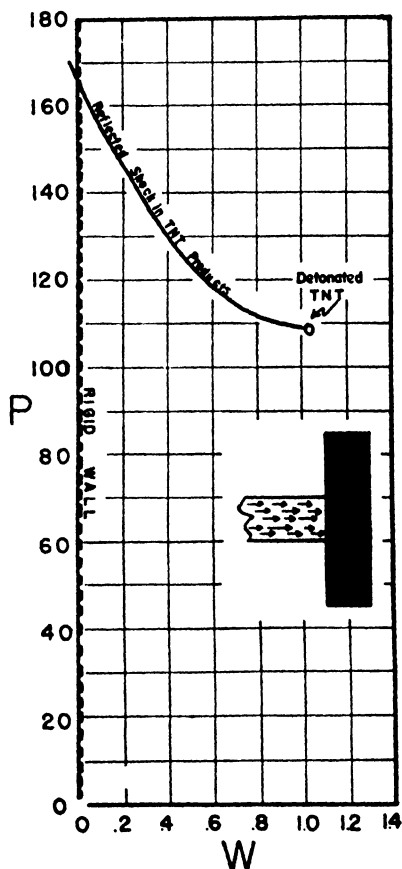
FIG. 49. P,W plot; TNT matched to rigid wall

The velocity W of the wall must be the component of its velocity normal to the shock front. Thus for a wedge moving with forward velocity W if the half angle of the wedge is β, the wall velocity is

$$W = W' \sin \beta \sec \left[\sin^{-1} \left(\frac{D}{W'} \right) - \beta \right]$$ (F12)

Example: Asymmetric initiation

Following the observation by Herzberg and Walker that a detonation wave does not spread as a perfectly spherical wave from its point of initiation (the

phenomenon gives rise to a "hook" in rotating-mirror photographs), Boggs and Strecker have made a series of experiments which demonstrate that the initiation process is indeed asymmetric. Each new portion of explosive is found to be initiated at its highest velocity in the direction of propagation of the initiating wave, and the wave will only with difficulty propagate around a corner. We shall return in a moment to a discussion of the numerical results obtained by Boggs and Strecker.

If it be supposed that the velocity measured in these experiments is merely the initial velocity of the shock wave set up in the receiver charge, the results can be explained beautifully in terms of the matching theory. We idealize the experimental situation slightly: Suppose a spherical portion of detonated explosive, with all fluid velocities in the same direction, to be embedded in a large
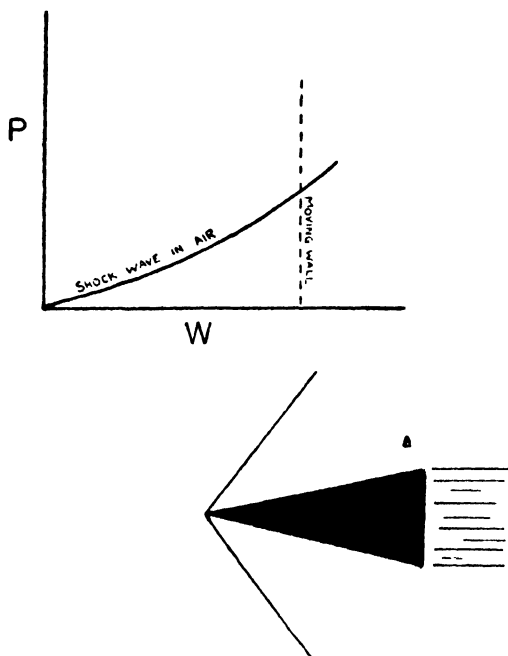
FIG. 50. Shock wave due to moving wall

intact portion of the same explosive. What then will be each point of the sphere?

The model for this problem, and the P,W graphs for its solution, are given in figure 51.

For the detonation wave in the intact explosive, assumed to be TNT of density 1.67, the curve is calculated by equation F1 with the numerical values:

$$P_0 = W_0 = 0$$

$$V_0 = 0.600 \text{ cm.}^3 \text{ g.}^{-1}$$

$$\alpha = 0.4225 \text{ cm.}^3 \text{ g.}^{-1}$$

$$\gamma = 1.24$$

For the rarefaction wave in the initiating explosive, assumed to be detonated TNT, the curve is calculated by equation F10 with the values $W_0 = 1.02 \cos \theta$ km. sec.$^{-1}$ and other numerical parameters as in previous examples.

From the points of intersection obtained in figure 51, a velocity is obtained for propagation at any angle to the direction of propagation of the initiator. The resulting velocities are presented graphically in figure 52, as percentages of the forward velocity. Also included in figure 52 are the experimental data by Boggs and Strecker listed in table F1, for pressed TNT of density 1.48, initiated by a train of the same TNT.
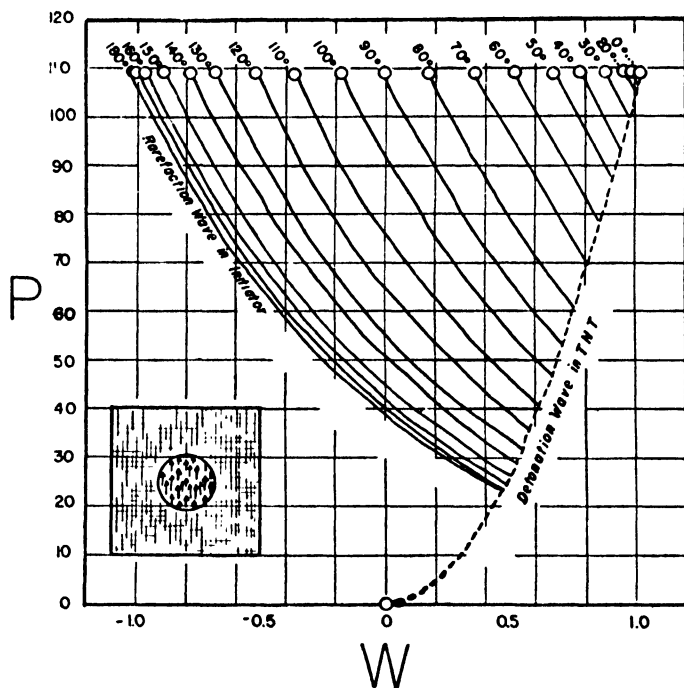
Fig. 51. P,W plot; initiator matched to TNT

The agreement between theory and experiment is quite striking, and leaves little doubt that the observed phenomena are due to asymmetric initiation of the kind discussed.

As figure 52 shows, the resulting wave does resemble a spherical wave sent out from a center of initiation projected somewhat ahead of the true center of initiation. Herzberg and Walker were led by this resemblance to propose that the wave propagated as a "low-order detonation" to this point, where it went over into a high-order detonation which then was propagated spherically.

The theory here developed lends strong support to the former of the two explanations.
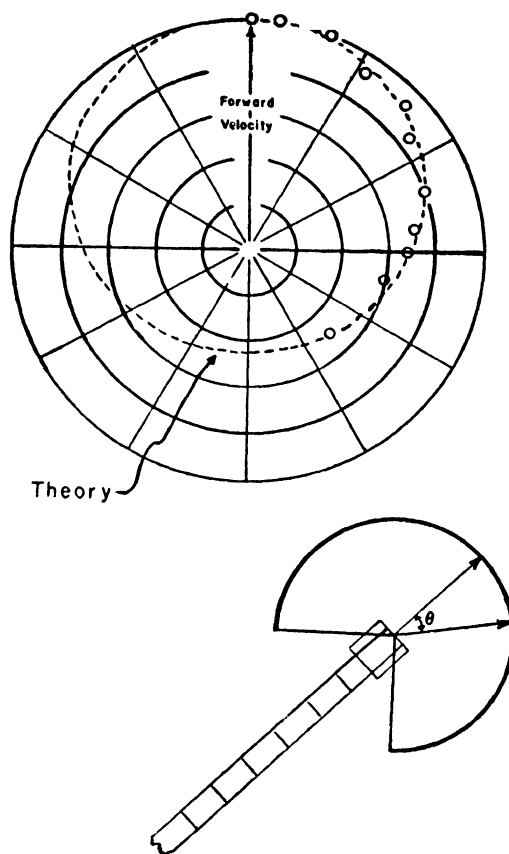
FIG. 52. Asymmetric initiation

TABLE F1

Data for pressed TNT of density 1.4

TYPE OF CHARGE	ANGLE	VELOCITY
		m. sec.$^{-1}$
Hemi-cylinder...........................	0°	6300
	7	6300
	32	5800
	54	5300
	82	4500
	90	4300
Three-quarter-cylinder........	0°	6300
	20	6300
	46	5800
	70	5000
	102	3850*
	135	3150*

* Computed from time lag given by the authors.

APPENDIX G. RATE LAWS OF SURFACE-BURNING REACTIONS

It is of some interest to find the dependence of extent of reaction on time, for topochemical reactions of the surface-burning type, in which the *linear* rate of burning is constant.

Example 1: Sphere uniformly ignited over its surface

Here the boundary between burned and unburned material is given by

$$\frac{R}{R_0} = 1 - \frac{t}{\tau} \tag{G1}$$

and the fraction of material reacted is obviously

$$N = 1 - \left(\frac{R}{R_0}\right)^3 \tag{G2}$$

Therefore the rate law in its integrated form is

$$N = 1 - \left(1 - \frac{t}{\tau}\right)^3 \tag{G3}$$

Example 2: Sphere ignited at its center

Here the boundary between burned and unburned material is given by

$$\frac{R}{R_0} = \frac{t}{\tau} \tag{G4}$$

and the fraction of material reacted is obviously

$$N = \left(\frac{R}{R_0}\right)^3 \tag{G5}$$

Therefore, the rate law is

$$N = \left(\frac{t}{\tau}\right)^3 \tag{G6}$$

Example 3: Sphere ignited at one point on its surface

Here the boundary between burned and unburned material is given by

$$\frac{R}{R_0} = 2\frac{t}{\tau} \tag{G7}$$

The fraction of material reacted is found by a simple integration to be

$$N = \frac{1}{2}\left(\frac{R}{R_0}\right)^3 - \frac{3}{16}\left(\frac{R}{R_0}\right)^4 \tag{G8}$$

Therefore, the rate law is

$$N = \left(\frac{t}{\tau}\right)^3 \cdot \left[4 - 3\frac{t}{\tau}\right] \tag{G9}$$

The dependence of N on t has been plotted in figure 53 for these three examples.

III. Detonation Initiated by a Mild Blow

A. Formulation of Problem: the "Internal Burning" Model

If a small fragment of explosive is placed on an anvil and struck a smart enough blow with a hammer, it will explode with a sharp report. When this same experiment is carried out in a machine under quantitatively controlled condi-
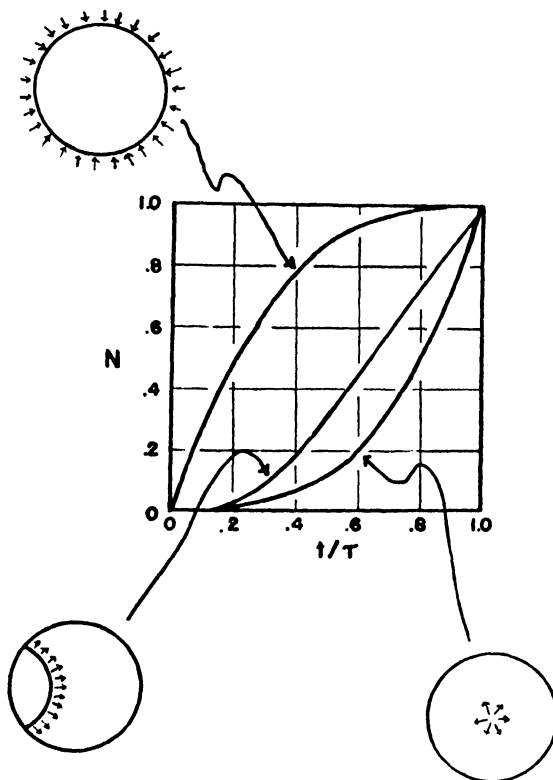
Fig. 53. Burning rate for various models

tions (thus a known weight of explosive, under controlled confinement, on a large rigid anvil, struck by a hammer of known weight falling from a measured height), it becomes the *drop test*. The drop test is universally used and is of first importance as a routine test for characterizing the sensitivity of explosives.

Two difficulties (of a primarily experimental nature) in drop testing have not yet been completely resolved.

In the first place, what is the criterion for "detonation" in a drop test? It is often remarked that the unaided human ear cannot distinguish between the noise of a true detonation and the noise of a very rapid partial burning. Certain

it is that an explosive under the hammer can give a loud report while (a) a good fraction of it remains undecomposed and (b) it is unable to initiate an adjacent portion of the same explosive not under the hammer. A more accurate statement of the situation is that there is no true boundary line between "rapid burning" and "detonation". Any rapid local chemical reaction will send out a sound wave of finite amplitude (generally a shock wave), and the intensity of this wave will be greater, the greater the amount of reaction and the shorter the time required for reaction. Further, even a shock wave of low intensity will in general be able to cause initiation at a few sensitive points before it has attenuated too much, a shock of greater intensity will merely remain able to cause initiation over a larger region.

Thus any rapid burning will in principle lead to a detonation—albeit a failing detonation. (If one chooses to restrict the term "detonation" to a *stable detonation*, one which will continue to propagate, then the dimensions and confinement of the charge through which propagation is to be measured must be specified; see discussion in Section II D.) It seems natural to measure the results of a drop test not as "detonates" or "does not detonate" but in terms of some variable which assumes a continuous range of values. One step in this direction is the measurement of the fraction of explosive decomposed under the hammer (by means of the volume of gas evolved: the Rotter Test Machine). Another is the use of a microphone arrangement to replace auditory observation (developed at the Explosives Research Laboratory, Bruceton).

In the second place, if the drop test on a particular explosive be repeated under identical conditions, it will sometimes give detonation and sometimes not. It becomes necessary to carry out at each height of fall enough experiments so that the results have statistical meaning. Suitably, from a graph of the data on probability paper, it is then possible to report the height of fall producing 10 per cent shots, 50 per cent shots, and 90 per cent shots (or any desired percentage of shots). The fact that sensitivity tests exist which do not show this large statistical scattering of data (namely, shock sensitivity tests such as cardboard gap tests) leads one to suppose that the fluctuations in drop tests are fluctuations in the operation of the machine, not fluctuations in the explosive preparation.

Yet even granting that drop testing involves some difficulties on the experimental side, one key fact is inescapable: A detonation can be started in an explosive by a hammer blow.

In comparison with the blow delivered by another detonating explosive, any blow delivered by a falling hammer is a mild blow. For the material velocity of an explosive is of the order of 1 km. per second, and an explosive will not be initiated by a shock wave whose material velocity is less than a fraction (say one-third to one-half) of that, while a hammer falling from a typical height of 1 m. will have a velocity of only 4.4 m. per second, or far less than sonic velocity in the explosive. So slow is the motion of the falling hammer that we can for practical purposes assume that stresses produced by the hammer are macroscopically uniform through the sample. The problem is thereby simplified to one involving the application of static stresses.

It is perfectly possible to carry out an impact test with a striking hammer whose velocity is 1 km. per second by dropping a bomb from an airplane onto a hard surface, or by mounting explosive in the nose of a rocket projectile and firing it against a concrete target, or by using as striker a high-velocity rifle bullet (R. J. Finkelstein). Such impact tests are better considered as true shock tests than as hammer-blow tests.

As a preliminary to a quantitative theory of initiation by a mild blow, it is first necessary to know the site of action of the mechanical stress. Experimental evidence, cited in detail below, indicates that the stress is concentrated at load-bearing contact points distributed uniformly through the bulk of the explosive.

1. Mass vs. energy relation

It was first proposed by Taylor and Weale (68) that the kinetic energy of the drop hammer required to produce a detonation was proportional to the mass of the explosive sample. Figure 54 presents Taylor and Weale's data for
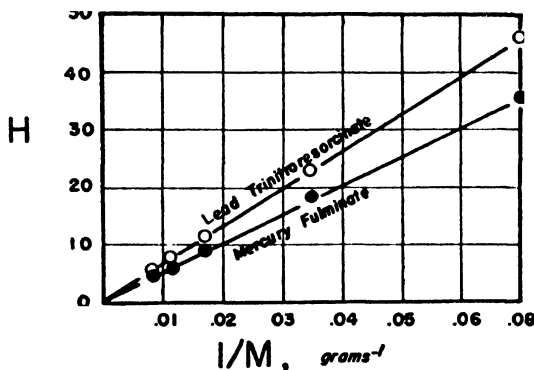
FIG. 54. Drop heights (H, fall in centimeters) for 50 per cent shots (Taylor and Weale (68))

the 50 per cent heights necessary to ignite a fixed amount of (a) mercury fulminate and (b) lead trinitroresorcinate with hammers of varying masses; the results indicate that the product MH (thus the kinetic energy of the falling hammer), rather than either mass or height alone, is critical in determining ignition. Figure 55 presents Taylor and Weale's data for the energies necessary to ignite varying amounts of an explosive consisting of mercury fulminate, potassium chloride, and antimony sulfide; here the amount of explosive was varied by changing the area of the end of the striking pin.

The proportionality of energy to mass in laboratory ignition tests has been confirmed for a large number of explosives by Lawrence (see figure 57 and discussion below).

The proportionality holds over a range of explosive mass from a few centigrams to 100 g., as shown by measurements on the 17 per cent energy for TPX (figure 56.) It can be observed from figure 56 that the proportionality of energy to mass is not rigid, the requisite energy density being somewhat less with the large charges. This is probably best interpreted as a time effect: The total time

of impact is longer for the heavier impacts, and it is reasonable to suppose that somewhat less energy is required for detonation if the explosive be maintained under stress for a longer time.
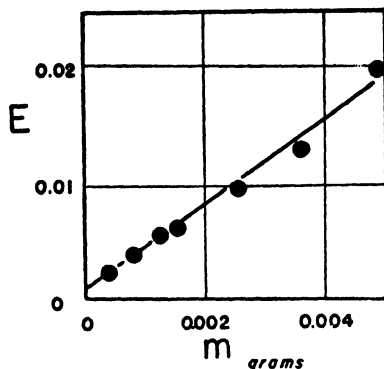
FIG. 55. Drop-weight energy for 50 per cent shots (E in calories)
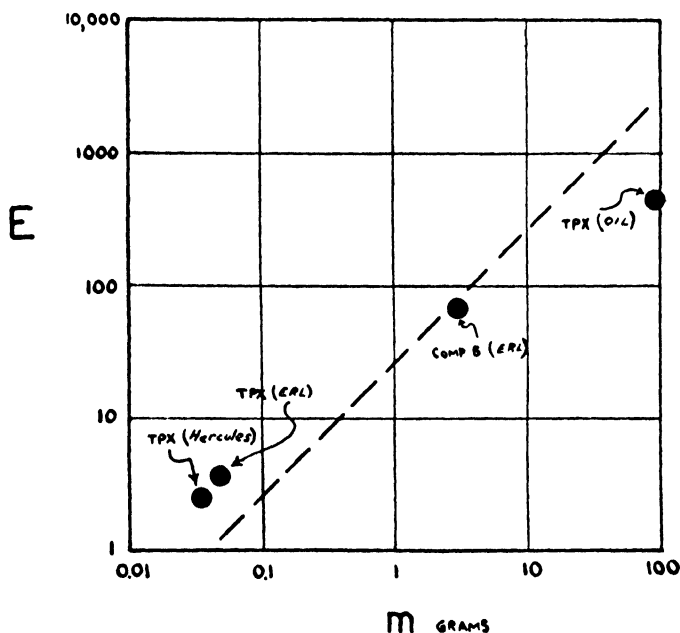
FIG. 56. Energy *vs.* mass for drop tests (E in calories for 17 per cent shots)

The statement that the energy necessary to cause initiation is proportional to mass must be qualified in two minor respects: (*a*) Since some portion of the energy of the hammer will always be lost into the anvil, and by rebound of the hammer, and perhaps by heating of a portion of the explosive which does not lead to reaction, the energy *vs.* mass relation plot remains linear but will have

an intercept corresponding to a finite energy requiremert even for zero mass of explosive. Figure 57 presents data by Lawrence to illustrate this effect. (*b*) It has been assumed that the machine itself does not produce any concentration of stress. The casing of an actual bomb may, by acting as a compound beam, produce highly concentrated local stresses when subjected to impact. This possibility may have a bearing on the few instances in which accidental bomb drops of a few feet have led to explosions.

The proportionality of energy of the falling hammer to mass of explosive must be interpreted to mean that the initiating effect of the stress is exerted throughout the *bulk* of the explosive. Initiation is not a surface effect. Neither
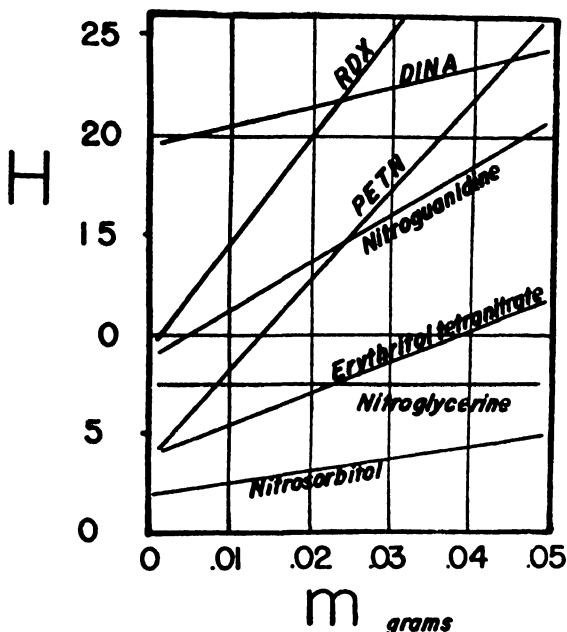
Fig. 57. Height *vs.* mass for shots (*H*, fall in centimeters of 2-kg. hammer for 50 per cent shots).

is it an accident which occurs at only a single point in the explosive; for if this were so, at a constant energy density a sample of explosive of twice the size would have twice as great a chance of initiation.

2. Absolute energy density for initiation

The numerical value of the energy density necessary to cause 50 per cent detonations varies from explosive to explosive, but it is of the order of 25 cal. per gram for typical organic nitro compounds. Therefore, if the explosive were to be heated uniformly throughout by the energy of the blow, its temperature would rise by only some 70°C. Since such a temperature rise would have no effect on the explosive, it is clear that the stress must be so concentrated as to

produce local high temperatures at a number of highly favored spots. These "hot spots" will undoubtedly be the load-bearing contact points between grains, or the corresponding interfaces in the interior of polycrystalline materials.

As additional circumstantial evidence for the hot-spot hypothesis, it is to be noted that the addition of sharp, angular, stress-concentrating materials (powdered glass) makes explosives more sensitive to impact, while the addition of lubricants (waxes; water) makes explosives less sensitive to impact.

We may now summarize the theory of the site of action of the mechanical stress, developed (at least in its broad outlines) by Taylor and Weale, and now generally accepted by investigators in the field:

Mechanical stress is concentrated at spots distributed uniformly through the bulk of the sample, so that these spots become hot. At each hot spot chemical reaction begins, so that the entire bulk of explosive is subject to a sort of internal burning. If the chemical reaction then becomes fast enough, the internal burning goes over into a detonation.

This is the "internal burning" model for initiation in a drop test. Bowden and coworkers (12, 13) have actually observed that when liquid nitroglycerin is ignited by impact, the initiation begins as a tiny flame which only after a period of about 100 microsec. goes over into detonation.

It appears likely that when an explosive is ignited by a flame at its surface, losses will be so great that no pressure can be built up, and the explosive will burn quietly without detonating. Only if the burning is able to penetrate to the interior of the substantially intact explosive, thus producing internal burning, will conditions be right for a detonation.

In particularizing the site of initiation, mention has been made neither of the exact mode of heating nor of the kinetics of the chemical reaction in the presence of thermal and dynamical losses. It is these omitted details which really make up the kernel of the theoretical problem, which we may now attempt to solve.

B. APPROXIMATE SOLUTION OF THE PROBLEM

It is easy enough to write down the differential equations for the problem of a spreading exothermic chemical reaction with thermal conduction and with dynamical gains and losses (they are in fact the equations given in the footnote to equation I: 1b of this report). But the complete equations are so difficult as to be hopelessly insoluble.

Now the application of the mechanical stress requires some tens of microseconds in a typical drop test; there is then a time lag of some 100–1000 microsec. during which the burning is going on,[22] and finally the detonation wave itself traverses the sample in about a microsecond. It is therefore possible to visualize the process as occurring in three separate steps, and for purposes of computation to neglect the overlapping of one step by another. In the first step, the mechanical stress gives rise to a temperature distribution at each load-bearing contact point. In the second step, the chemical reaction spreads at a rate determined

[22] Oscillographic measurements of the time delay between impact and detonation.

by its rate–temperature law and the temperature distribution given by heat evolution and conduction. In the third step, the pressure produced by the products of burning gives rise to a detonation wave. The replacement of the actual process by these three successive processes simplifies the mathematical treatment to the extent that at least an approximate solution can be obtained for each process.

Step 1. Initial temperature distribution due to mechanical stress

To find the temperature pattern at a hot spot or contact point, it is necessary to know (1) the number of contact points and thus the total stress at any one contact point; (2) the stress pattern around a contact point; (3) whether the material under such a stress will behave elastically or will flow; (4a) if it behaves elastically, what temperature is produced by elastic compression at each region of the stress pattern; and (4b) if it flows, what will be the frictional heating.

Unfortunately, not one of the items in the list above is known. The number of hot spots might be estimated roughly from the geometry of the packing. But does the number change with the applied stress, or not? The finding of the stress pattern is a straightforward problem in stress analysis, once the geometry of the contact regions is known. Since these first two are essentially problems in static stresses, the methods of photoelastic analysis at once suggest themselves. The last three items require a knowledge of the stress-strain and viscous behavior of the substance, which is not excessively difficult to obtain by direct measurement (preferably on a non-explosive analog!).

In the complete absence of necessary data, about all that can be done is to assume arbitrarily a size and a temperature of the initial hot spot.

Step 2. The spreading exothermic finite chemical reaction with thermal conduction

In the above definition of the problem, "spreading" indicates that intact explosive substance is progressively heated and consumed; "exothermic" that the chemical reaction evolves heat (but the dynamical effect of any pressure change is neglected); "finite" that the amount of explosive in any one region is not limitless, so it does not keep evolving heat forever; "thermal conduction" that heat is conducted away from the zone of reaction into the cooler intact explosive.

The integro-differential equation governing this process is, for spherical symmetry,

$$\frac{\partial(rT)}{\partial t} = \frac{\kappa V}{C_v}\frac{\partial^2(rT)}{\partial x^2} + \frac{Z\Delta Q}{rC_v}e^{-\Delta H^{\ddagger}/R_0 T}\,e^{-\int_0^t Z e^{-\Delta H^{\ddagger}/R_0 T}\,dt} \tag{1}$$

where the reaction rate has been assumed to obey the law

$$\frac{dN}{dt} = (1 - N)Z e^{-\Delta H^{\ddagger}/R_0 T} \tag{1a}$$

In equation 1 the first term on the right gives the conduction of heat, while the second term gives the heat produced by reaction; the first exponential

factor contains the dependence of reaction rate on temperature, and the second exponential factor takes into account the finite amount of the reacting substance.

We have attempted to solve equation 1 by a point-by-point graphical integration, in order to obtain a general idea of the behavior of the process. But this integration is so excessively tedious that it has been abandoned. The results of a particular computation are given in figure 58, from which it will be seen that the reaction is beginning to progress in the originally intact explosive.
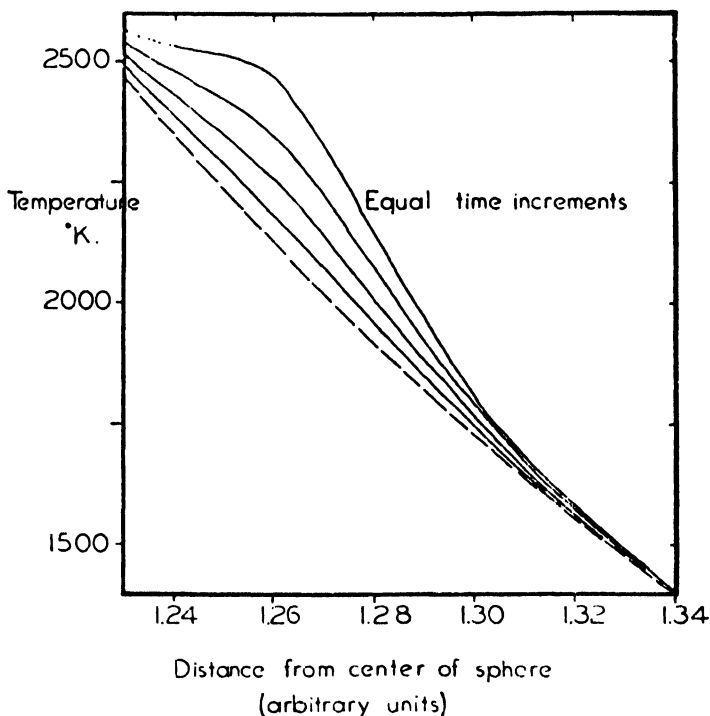
Fig. 58. Numerical integration of initiation problem

The numerical parameters used in this integration were as follows: Initial temperature as given by a dashed line; this is the temperature distribution appropriate to heat spreading from an instantaneous point source.

$$\frac{\kappa V}{C_v} = 0.003 \text{ cal. cm.}^{-1} \text{ sec.}^{-1}$$

$$V = 0.667 \text{ cm.}^3 \text{ g.}^{-1}$$

$$C_v = 0.5 \text{ cal. g.}^{-1}$$

$$\Delta Q = 600 \text{ cal. g.}^{-1}$$

$$Z = 10^{13} \text{ sec.}^{-1}$$

$$\Delta H^{\ddagger}/R_0 = 17,000 \text{ deg.}$$

Since the complete equation for the process cannot practicably be solved, the next move is to drop one or more requirements of the original problem, in the hope that the simpler problem will be soluble.

(2a) *The exothermic chemical reaction with thermal conduction:* Here the requirements have been relaxed that the chemical reaction spread and that it be finite. The model is of a small hot sphere of uniform internal temperature; reaction proceeds only within this sphere; heat is conducted away by the surrounding medium. This problem has been attacked by Rideal and Robertson, who find that the appropriate sizes and temperatures of hot spots such that the rate of heat production shall just balance the rate of heat conduction are as given in table 14.

As will be seen from table 14, the calculated critical hot-spot temperature is very sensitive to the assumed hot-spot radius.

(2b) *The spreading finite chemical reaction with thermal conduction:* Here the requirement that the reaction be exothermic has been relaxed. Because of the absence of sources, the problem is easy to solve. The temperature as a function of time and distance can be found by the classical methods for heat conduction

TABLE 14

Critical hot-spot temperature for hot-spot radius as listed

EXPLOSIVE	$r = 10^{-3}$	10^{-4}	10^{-5}	10^{-6} CM.
	°C.	°C.	°C.	°C.
PETN	310	385	495	640
RDX	380	485	615	815
HMX	410	510	645	825
Tetryl	425	570	815	1250
Ammonium nitrate	530	825	1230	2180

problems. Then the amount of reaction at any point must be found by numerical integration of the rate law, as is customary in reaction-rate problems with varying temperature.

Figure 59 presents the calculated extent of reaction for this model, the heat spreading from an instantaneous point source of 10^{-10} cal. strength. It will be noted that the reaction proceeds at about the rate at which the heat spreads, then ceases abruptly when the temperature becomes too low to initiate reaction. Numerical parameters for computation of figure 59 were the same as those for figure 58.

(2c) *The finite exothermal chemical reaction:* Here the requirements that the reaction spread and that heat is conducted away have been relaxed. This is just the problem of an exothermic reaction proceeding adiabatically (27).

If the rate law for the reaction is

$$\frac{dN}{dt} = (1 - N)Ze^{-\Delta H \ddagger / R_0 T} \tag{2}$$

and the extent of reaction N is given by

$$N = \frac{T - T_0}{T_1 - T_0} \tag{3}$$
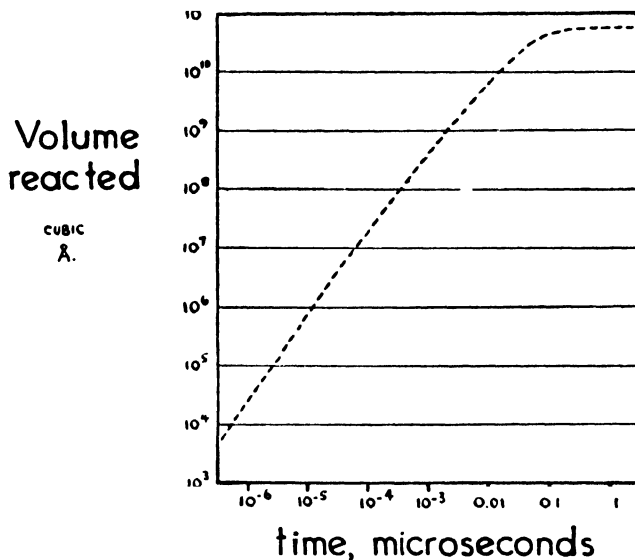
FIG. 59. Athermic spreading reaction rate

Then the rate law becomes

$$\frac{dT}{dt} = (T_1 - T)Ze^{-\Delta H^{\ddagger}/R_0 T} \tag{4}$$

This may be integrated without difficulty to give

$$Zt = Ei\left(\frac{\Delta H^{\ddagger}}{R_0 T}\right) - Ei\left(\frac{\Delta H^{\ddagger}}{R_0 T_0}\right) + e^{-\Delta H^{\ddagger}/R_0 T_1}\left\{Ei\left(\frac{\Delta H^{\ddagger}}{R_0 T_0} - \frac{\Delta H^{\ddagger}}{R_0 T_1}\right)\right.$$
$$\left. - Ei\left(\frac{\Delta H^{\ddagger}}{R_0 T} - \frac{\Delta H^{\ddagger}}{R_0 T_1}\right)\right\} \tag{5}$$

where

$$Ei(x) = \int_{-\infty}^{x} \frac{e^y \, dy}{y} \tag{5a}$$

for which tabulated values are available. For all values of T except those in the immediate neighborhood of T_1, the exponential integral may be replaced by its approximate value

$$Ei(x) \approx \frac{e^x}{x}$$

giving as a final result

$$t = \frac{R_0}{Z\Delta H^{\ddagger}}\left\{\frac{T_0^2}{T_1 - T_0}e^{-\Delta H^{\ddagger}/R_0 T_0} - \frac{T^2}{T_1 - T_0}e^{-\Delta H^{\ddagger}/R_0 T}\right\} \tag{6}$$

Figure 60 presents the extent of reaction as a function of time for the adiabatic exothermal reaction, as computed from equation 6, for the same reaction rate used in computing figures 58 and 59. The general course of the reaction resembles a long inhibition period followed by a rapid completion of the reaction.
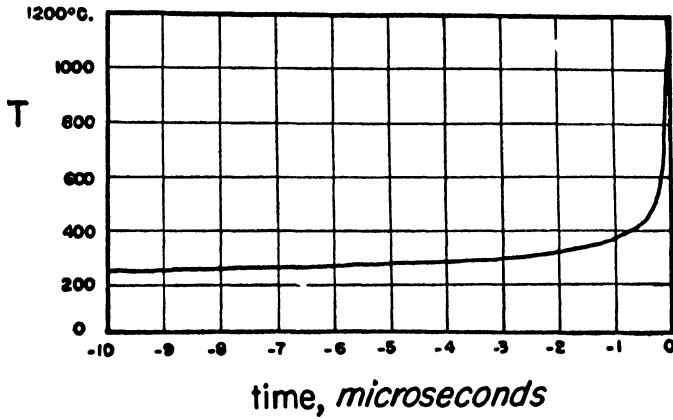
FIG. 60. Exothermic adiabatic reaction rate
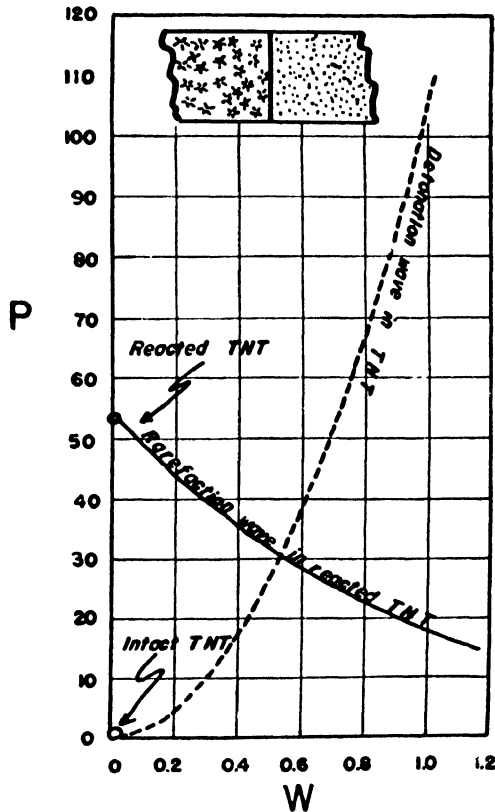
FIG. 61. TNT matched to TNT; D,W plot

The various approximate calculations listed above do not give a very satis-
factory picture of the course of a spreading reaction of the type described.

This is a sufficiently fundamental problem in reaction kinetics so that a thorough investigation of it would be useful. From the theoretical side, such a study has not yet been made. From the experimental side, it may be possible to study the kinetics of the spreading reaction by a technique such as quenching the reaction after various elapsed times. In such an experimental investigation, it would of course be necessary to control the initial temperature pattern at each hot spot.

Step 3. The detonation wave set up by pressure

The exact solution of the hydrodynamic equations for the process by which internal burning goes over into detonation is very difficult. We propose, instead, an heuristic approach to the problem.

In the first place, consider a quantity of explosive undergoing static reaction—burning. Let another quantity of intact explosive be placed adjacent to it. Under what conditions will the burning substance *most effectively* set up a shock wave in the intact substance? Clearly, these conditions are (1) the burning substance is of infinite dimensions, (2) the intact substance is of infinite dimensions, and (3) the entire burning process is completed instantaneously. For under any other conditions, losses will supervene to cut down the intensity of the shock wave.

The mathematical tools are at hand to find precisely this most effective shock (see appendix F of this report). Figure 61 presents the details of the solution, for reacted TNT against intact TNT.

The shock curve in intact TNT was computed according to equation F1 with

$$P_0 = W_0 = 0$$

$$\gamma = 1.24$$

$$V_0 = 0.600 \text{ cm.}^3 \text{ g.}^{-1}$$

$$\alpha = 0.4225 \text{ cm.}^3 \text{ g.}^{-1}$$

The rarefaction curve in reacted TNT at rest was computed according to equation F10 with

$$W_0 = 0$$

$P_0 = 54,500$ atm.; this
      is one-half the detonation
      pressure, as pointed out
      in Section I

$$C_0 = 3.58 \text{ km. sec.}^{-1}$$

$$\gamma = 1.24$$

$V_0 = 0.600$ cm.^{3} g.$^{-1}$ (reaction at
      constant volume)

$$\alpha = 0.4225 \text{ cm.}^3 \text{ g.}^{-1}$$

From the point of intersection of the two curves, the detonation velocity is computed to be 53 per cent of the ideal detonation velocity for TNT.

A velocity of 53 per cent of the ideal velocity is therefore the best that can be done if burned TNT at rest is initiating intact TNT. A similar computation can be made for any explosive.

Is now a shock velocity of 53 per cent D_i sufficient to initiate a stable detonation in TNT? By referring to the discussion of failure (Section II D) we see that such a velocity is able to produce stable detonation if the radius of the receiver charge is no less than two reaction zone lengths (of the receiver substance). However, the wave of this velocity is on the verge of being too weak to initiate a stable detonation; if the velocity should fall to, say, one-half this velocity, it would almost certainly fail to initiate detonation. We may say that the initiation is precarious.

For some explosives, the maximum shock producible by static burning might be less than the minimum shock which would produce stable detonation. Such an explosive could not be detonated at all in a drop test. Ammonium nitrate is perhaps such an explosive.

We can proceed to remove, one by one, the restrictions under which the most effective wave was computed

(1) *Length and width of receiver charge:* If the length of the receiver charge is not at least several of its own ideal reaction zone lengths, it will not be possible to observe whether the wave is building up; but this restriction is somewhat trivial. Likewise, if the receiver charge is of less than the critical radius, it will of course not propagate stably. The receiver charge must therefore be of radius at least two of its own ideal reaction zone lengths, preferably more.

(2) *Width and length of initiator charge:* If the burned material is of either finite width or length, a rarefaction wave will be superimposed on the shock wave and eat it away. To produce initiation, it is necessary to maintain the shock intensity in the receiver for a distance not less than the reaction zone length of the receiver substance. This will only be possible if the dimensions of the initiator charge are of this same order of magnitude.

Since what we have called the "initiator charge" is in reality the burned products arising from a collection of hot spots, or "super-hot-spot", we can write: *The minimum size of "super-hot-spot" which will initiate detonation is approximately the ideal reaction zone length of the substance to be detonated.*

It is particularly to be noted that a single hot spot, of less than 1 micron diameter, may (if its reaction is fast enough) outrun temperature losses and continue to burn. But only a much larger hot spot, say a "super-hot-spot" 1 mm. in diameter, will be able to outrun dynamical losses enough to initiate detonation in a typical organic nitro explosive.

(3) *Time of reaction:* Assuming that the super-hot-spot which acts as initiator is a sphere of the dimensions of the reaction zone length, any shock wave sent out by it into a non-reacting substance will fall to half its velocity within a distance of about that same magnitude. The time required to build up the pressure must therefore be not more than the time for the wave to traverse this

distance, which is the reaction time τ of the receiver charge. For typical organic nitro explosives, this is about 1 microsec. We can write: *Of the pressure increase produced by burning, only the increment of pressure over about one reaction time of the substance to be detonated can be utilized for initiation.* Any pressure which is produced more gradually simply appears as hydrostatic pressure, which is not useful for initiation.

This result indicates that it is undesirable for any appreciable amount of the explosive in the super-hot-spot to have burned in the long time-lag preceding detonation, for such burned explosive cannot contribute pressure to the initiation. On the other hand, it is very desirable for the explosive in the super-hot-spot to show a long induction period and then to decompose all at once. One way in which this could arise would be for the reaction to spread over the internal surface throughout the region originally heated by mechanical stress; for this would lead to burning ignited over a large region before any appreciable amount of explosive had been consumed. (The possibility is suggested of *chemical* sensitizing and desensitizing of the surface of explosives, as a means of controlling their impact sensitivity. This experiment is to be distinguished from *mechanical* sensitizing and desensitizing, as by sharp grains or by lubricants, respectively.)

It is interesting to point out that the familiar technical design for initiation of explosives—namely, primer ‖ booster ‖ explosive—is beautifully designed to circumvent difficulties in initiation. The primer is a substance of very short reaction zone, and usually of well-defined sharp-edged crystals (often metallic or metal-organic salts), so that it is easily detonated by a mild hammer blow. The booster is an explosive whose reaction zone length is of the same order as the dimensions of the primer, so it is readily detonated by the primer. The dimensions of the primer are, in turn, of the order of the reaction zone length of the substance which comprises the main explosive charge, so the latter is readily detonated.

In summary, we may outline the procedure to be followed in the proposed theoretical analysis of sensitivity toward impact, for a particular experimental situation:

(*1*) The macroscopic stress pattern due to the falling weight must be determined. For an ordinary drop test the stress is uniform, but in a more general experiment it might not be uniform. From the macroscopic stress pattern, the microscopic stress pattern is then found for each load-bearing contact point. From the microscopic stress and the time of its application, the amount of heating at each contact point is determined. It seems likely that most of the heating will turn out to be due to flow and frictional heating, rather than to reversible compressive heating, but this point must be checked for each individual case.

(*2*) From the initial temperatures and the kinetics of the burning reaction, the rate of reaction must be found as a function of time. As pointed out above, the kinetics of such reactions are not now satisfactorily known, so they will have to be determined. It is to be noted that the burning process will not only come to a stop if thermal conduction outruns it, but will also largely stop when the pressure is released by the removal of the hammer.

(*3*) The maximum increment of pressure produced by the burning over any 1-microsec. time interval is found. If the magnitude of this pressure increment is enough to produce a minimum initiating shock, while also the size of the spot producing it is as great as a reaction zone length in the explosive to be detonated, than a stable detonation will be produced.

At the present time, our knowledge of the internal stresses in a polycrystalline material under load is very slight. The theoretical treatment of heating by an applied stress (thus of the dissipation of energy) has not been developed to a degree that it could immediately be applied to our problem. The theory of the kinetics of spreading exothermic reactions is in a completely unsatisfactory state. The present theory of reaction zone lengths and the matching of shock waves at boundaries does seem to be in a satisfactory state, but even here our numerical knowledge is limited to the examples given in Section II of the present report.

It is evident from the foregoing remarks that the complete theory of initiation by impact must wait upon a thorough theoretical and experimental program of study of stress heating, burning reactions, and reaction zone lengths in high explosives.

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THE REACTIONS OF MONOMERIC STYRENES

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CONTENTS

Even before its structural formula was known, Kopp (411) in 1844 and Blyth and Hofmann (87) in 1845 had examined certain chemical reactions of monomeric styrene. They reported that treatment with nitric acid yielded nitrostyrene, oxidation yielded benzoic acid, and treatment with chlorine or bromine yielded halogen addition products. After 1866, when Erlenmeyer (203) suggested that styrene was phenylethylene, the nature of these reactions became clearer. Subsequent experimenters have, of course, substantiated this formula in numerous ways and have added a host of reactions to those examined by the earliest investigators.

In considering the chemistry of styrene and its derivatives, the name "phenylethylene," used by Erlenmeyer to describe its structure, must be kept continually in mind. Styrene is a typical olefinic hydrocarbon and undergoes a great variety of reactions characteristic of compounds containing a carbon–carbon double bond. However, the phenyl group exerts a marked activating influence on this functional group, as is shown by the pronounced tendency for the compound to polymerize. Styrene readily undergoes a number of reactions which other, less reactive olefins undergo with difficulty or not at all.

The present review describes the reactions of monomeric styrenes. It includes nothing on the polymerization of styrene or its derivatives. The chemistry is limited to compounds having only two carbon atoms in the functional group attached to the benzene ring. α-Methylstyrene, β-methylstyrene, cinnamyl alcohol, cinnamaldehyde, cinnamic acid, etc. have been omitted purposely, as falling outside the scope of this review. Similarly the nuclearly substituted styrenes have been limited to those containing one benzene ring. This excludes purposely vinylnaphthalene, vinylbiphenyl, etc. Even with these artificial limitations the field covered is a large one. The literature has been covered as completely as possible through December 31, 1947 and a number of references have been added which have appeared since then.[1]

Nomenclature

The names "cinnamene," "phenethylene," "phenylethylene," "styrol," and "vinylbenzene" appear in the literature. At present in *Chemical Abstracts* styrene and its substitution products are indexed under *styrene* and the positions of substituents are indicated as follows:

$$(p) \; 4 \underset{\substack{3 \quad 2 \\ (m) \quad (o)}}{\overset{\substack{5 \quad 6}}{\diamondsuit}} \!\!-\!\!CH\!\!=\!\!CH_2$$
$$\qquad\qquad\qquad (\alpha)\quad(\beta)$$
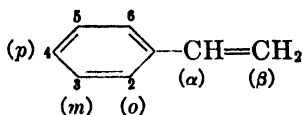
[1] Some additions inserted in manuscript to August 15, 1949.

I. REDUCTION

A. Catalytic hydrogenation

The most straightforward method of reduction is the direct addition of one or more molecules of hydrogen in the presence of a catalyst. In 1868 Berthelot (81) passed a mixture of styrene and hydrogen through a hot tube and detected ethylbenzene among the products of the reaction. However, under the conditions used (73, 79) pyrolysis predominated, so that the principal compounds isolated were benzene and ethylene together with smaller amounts of acetylene, toluene, and p-xylene.

In 1901 Sabatier and Senderens (644) studied the vapor-phase catalytic hydrogenation of styrene. When copper was used as the catalyst, ethylbenzene was formed, whereas over a nickel catalyst ethylcyclohexane, contaminated with a little methylcyclohexane, was obtained. Willstätter and King (779) used platinum as the catalyst and acetic acid as the solvent. Depending on the duration of the hydrogenation either ethylbenzene or ethylcyclohexane could be produced.
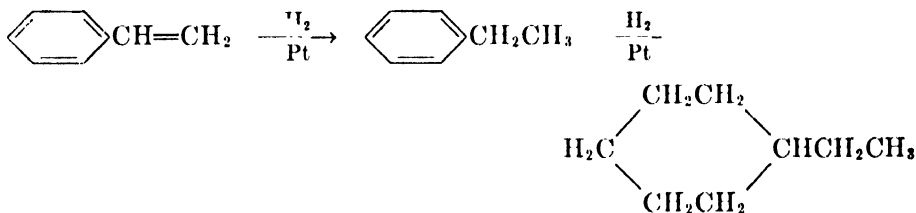
Since these early studies, a number of investigators have examined the reaction. Styrene has been hydrogenated to ethylbenzene in essentially quantitative yield in the presence of all the common hydrogenation catalysts. These include Raney nickel (176, 804), copper chromite (804), palladium black (771), platinum black (362, 438), platinum oxide (367), and palladium oxide (367). Copper is equally effective (403), and some reduction has been reported to take place in the presence of zinc, magnesium, aluminum, cupric chloride, zinc chloride, magnesium chloride, and aluminum chloride (403). These reductions in the presence of metal chlorides have not been confirmed. In fact, styrene reacts very readily with hydrogen, much more so than cinnamic acid, benzalacetone, or α-pinene (764, 765), and 900 times faster than benzene (458). Competitive hydrogenations of styrene with eugenol, oleic acid, and several other olefinic compounds have been studied (438, 439).

The heat of hydrogenation of styrene to ethylcyclohexane has been found to be −77,893 cal. per mole (164). The reaction rate is independent of styrene concentration, but proportional to the hydrogen pressure and to the platinum concentration (187). The reaction has, of course, served as an example in discussions of the theory of catalytic hydrogenation (148, 655).

Catalytic hydrogenation has proven equally effective for converting substi-

tuted styrenes to the corresponding ethylbenzenes. For convenience these reductions are summarized in tabular form (table 1).

v. Braun, Karpf, and Garn (113) reduced m-phenylenediacetonitrile with sodium and alcohol and then pyrolyzed the quaternary ammonium hydroxide obtained from the resulting amine. The product, which undoubtedly was a styrene, was reduced to the corresponding saturated aromatic hydrocarbon. Fries and Bestian (246) hydrogenated o-divinylbenzene in the presence of platinum oxide. Depending on whether one or two moles of hydrogen were absorbed, o-ethylstyrene or o-diethylbenzene was obtained.

TABLE 1

Hydrogenation of substituted styrenes

SUBSTITUTED STYRENE	CATALYST	YIELD	REFERENCE
		per cent	
o-Methyl................	Pd		(186)
p-Methyl........	Pd		(486)
m-Bromo......................	PtO₂	86	(125)
p-Phenoxy....................	Raney nickel	84	(234)
2,6-Dimethoxy................	Pt	69	(667)
2,5-Dimethyl-3,6-dimethoxy....	Raney nickel	86	(687)
4,5-Dimethoxy-2-carboxy.......	Pd		(406, 408)
o-(β-Dimethylaminoethyl)	Pd		(116)

With styrenes substituted in the side chain, hydrogenation proceeds in the normal manner if the substituent is not halogen. Thus, in the presence of palladium β-acetoxystyrene yielded 82.5 per cent of β-phenethyl acetate (678), in the

$$C_6H_5CH{=}CHOCOCH_3 \xrightarrow[Pd]{H_2} C_6H_5CH_2CH_2OCOCH_3$$
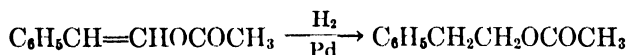
presence of platinum oxide α,β-diacetoxystyrene yielded styrene glycol diacetate (156), and in the presence of platinum p-methoxy-α-ethoxystyrene yielded α-ethoxyethylanisole (583). Similarly in the presence of platinum oxide β-diethylamino-, β-piperidino-, β-methylbenzylamino-, and β-dibenzylamino-styrenes yielded the corresponding ethylbenzenes (470). In the presence of a palladium catalyst the two latter compounds were debenzylated to give methyl-β-phenethylamine and β-phenethylamine, respectively.

$$C_6H_5CH{=}CHN{\Big\langle}^{CH_2C_6H_5}_{CH_3} \xrightarrow[Pd]{H_2} C_6H_5CH_2CH_2NHCH_3 + C_6H_5CH_3$$
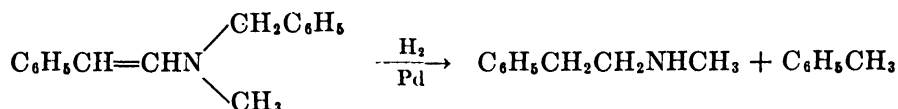
Treatment of N-methyl-N-β-(3,4-diacetoxystyryl)acetamide with hydrogen in the presence of palladium gave N-methyl-N-β-(3,4-diacetoxyphenyl)ethylacetamide (118).

The hydrogenation of N-methyl-N,β-styryl-p-toluenesulfonamide with a palladium catalyst proceeded normally to give N-methyl-N-β-phenethyl-p-toluene-

sulfonamide (375). N-Benzyl-N-β-styryl-p-toluenesulfonamide behaved similarly and N-β-styryl-p-toluenesulfonamide yielded N-β-phenethyl-p-toluenesulfonamide. In the presence of a platinum oxide catalyst sodium β-styrylsulfonate yielded sodium β-phenylethanesulfonate (373).

$$C_6H_5CH{=}CHSO_3Na \xrightarrow[\text{PtO}_2]{\text{H}_2} C_6H_5CH_2CH_2SO_3Na$$
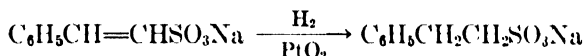
Styrenephosphonic acid was hydrogenated in the presence of a palladium on barium sulfate catalyst to give β-phenylethanephosphonic acid (66)

If the styrene contains halogen in the side chain, catalytic hydrogenation removes it whether it is in the active α- or the unreactive β-position. Thus, both p-methoxy-α-chloro- and p-methoxy-β-chloro-styrenes yielded p-ethylanisole on treatment with hydrogen in the presence of platinum (583).

$$CH_3O{-}\langle\ \rangle{-}CH{=}CHCl \xrightarrow[\text{Pt}]{\text{H}_2} CH_3O{-}\langle\ \rangle{-}CH_2CH_3$$
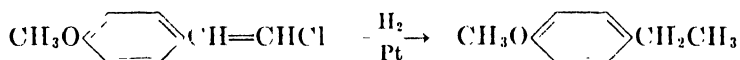
Similarly in the presence of palladium p-methoxy-β-chlorostyrene yielded 90 per cent of p-ethylanisole, 3,4-methylenedioxy-β-chlorostyrene yielded 65 per cent of 3,4-methylenedioxyethylbenzene, and β-bromostyrene yielded 62 per cent of ethylbenzene (99). When β-bromostyrene was treated with hydrogen at 140°C. in the presence of palladium, potassium hydroxide, and hydrazine hydrate in methanol solution, the product was 52 per cent of 1,4-diphenylbutadiene (132). This is really a coupling reaction but it is described here because the conditions are those of reduct .

B. Chemical methods of reduction

Again, Berthelot (1867) was the first to describe the reduction of styrene by chemical means (74, 77, 82). On treating the compound with hydriodic acid in a sealed tube at 280°C. ethylbenzene, plus a little benzene and ethane, was formed. With a larger excess of hydriodic acid the products were octane, a little hexane, and ethane. Stoermer and Kippe (711) later reported obtaining ethylbenzene by treating styrene with hydriodic acid. Under the same conditions they report o -phenoxystyrene as giving phenol and styrene diiodide, since their ultimate product was β-phenylnaphthalene.

$$C_6H_5CH{=}CHOC_6H_5 + 2HI \rightarrow$$

$$C_6H_5OH + C_6H_5CHICH_2I \rightarrow \langle\langle\ \rangle\rangle{-}C_6H_5$$
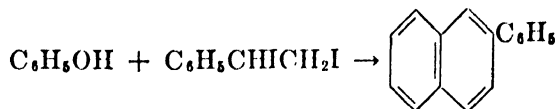
When heated to 200°C. with phosphorus and hydriodic acid, vinylmesitylene yielded mesitylene (393).

Klages and Keil (392) used sodium and alcohol very successfully for the reduction of styrene and its homologs. With styrene itself the yield of ethylbenzene was 82 per cent Other styrenes reduced by the same method are summarized

in table 2. While he does not say so specifically, Semmler (665) probably used sodium and alcohol to reduce β-acetoxystyrene to β-phenethyl alcohol. With sodium and alcohol β-phenoxystyrene gave a 65 per cent yield of ethylbenzene (710).
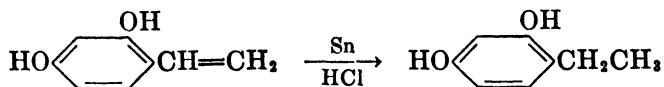
Sodium in liquid ammonia has been reported as a means of slowly reducing styrene to ethylbenzene (436). The yield given was 50 per cent, with polystyrene as the by-product (787). No reaction was obtained when styrene was treated with sodium amalgam and water (712); with this same reagent (o-vinylbenzyl)-trimethylammonium chloride yielded o-methylstyrene (188).

Metal and acid combinations have been utilized successfully for the reduction

TABLE 2

Reduction of styrenes with sodium and alcohol

STYRENE	YIELD	REFERENCE
	per cent	
p-Methyl		(186, 392)
2,4-Dimethyl	74	(392)
2,5-Dimethyl		(392)
2,4,5-Trimethyl	82	(392)
2,4,6-Trimethyl	90	(392)
p-Ethyl	85	(392)
2,5-Diethyl		(392)
2,4,5-Triethyl		(392)
p-Isopropyl		(392)
o-Methoxy		(390)
m-Methoxy		(390)
p-Methoxy		(390)
p-Ethoxy		(390)
3,4-Methylenedioxy		(390)

of substituted styrenes. Thus, 4-vinylresorcinol has been reduced to 4-ethyl-resorcinol with tin and hydrochloric acid (223). Similarly, N-methyl-N-β-styryl-

$$\text{HO}\langle\bigcirc\rangle\text{CH}{=}\text{CH}_2 \xrightarrow[\text{HCl}]{\text{Sn}} \text{HO}\langle\bigcirc\rangle\text{CH}_2\text{CH}_3$$
(with OH substituent on each ring)

p-toluenesulfonamide was reduced to N-methyl-N-β-phenethyl-p-toluenesulfon-amide with iron and alcoholic hydrochloric acid (375). Zinc and acetic acid have been used to reduce what was probably 2-carboxy-4-methoxy-β,β-dichlorostyrene to 2-ethyl-5-methoxybenzoic acid (321) and a compound postulated as 2-methyl-4-methoxy-5-carboxy-α-hydroxy-β,β-dichlorostyrene to 2-hydroxy-4-methyl-5-ethylbenzoic acid (666).

On the other hand, since stannous chloride and hydrochloric acid have no effect on the vinyl group in styrene, this reagent may be used for the reduction of other groups in the styrene molecule. These reactions are discussed in detail in the section devoted to reactions not involving the vinyl group.

C. Reduction of β-nitrostyrenes

Because of the importance of β-phenethylamines in biological and medicinal chemistry and because of their utility as starting materials for the synthesis of isoquinolines, the preparation of these compounds by the reduction of β-nitrostyrenes has occupied the attention of many chemists. The wide applicability of such a synthesis from the requisite aromatic aldehyde is obvious:

$$ArCHO + CH_3NO_2 \rightarrow ArCH{=}CHNO_2 \xrightarrow{(H)} ArCH_2CH_2NH_2$$
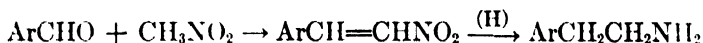
Unfortunately the reduction proved extremely difficult and it was a long time before it could be effected in good yields.

In 1873 Alexeyev (13), the first investigator in the field, treated nitrostyrene with sodium amalgam and isolated a red oil which might have been azostyrene. A red solution was obtained by treating nitrostyrene with zinc and alcoholic sodium hydroxide. Priebs (571), who first elucidated the chemistry of β-nitrostyrene, was unable to isolate anything from reduction experiments.

Bouveault and Wahl were the first to make any progress with the problem. In 1902 they reported obtaining p-methoxyphenylacetaldehyde and 3,4-methylenedioxyphenylacetaldehyde by treating the corresponding β-nitrostyrenes with zinc and acetic acid (107). Later the intermediate phenylacetaldoxime was isolated after treating β-nitrostyrene with aluminum amalgam or zinc and acetic acid (106). The yield when zinc and acetic acid in ether was used was 22 per cent (108).

$$ArCH{=}CHNO_2 \xrightarrow[C_2H_5COOH]{Zn} ArCH_2CH{=}NOH \xrightarrow{H_2O} ArCH_2CHO$$

Medinger (488) reduced 3,4-methylenedioxy-β-nitrostyrene with zinc and aqueous acetic acid and obtained a 70 per cent yield of 3,4-methylenedioxyphenylacetaldoxime. Zinc and ammonium chloride also was used successfully, but aluminum amalgam was not active. Rosenmund obtained a 20 per cent yield of p-methoxyphenylacetaldoxime as well as a little p-methoxy-β-phenethylamine by treating p-methoxy-β-nitrostyrene with aluminum amalgam in moist ether (673). With zinc and alcoholic acetic acid the yield of oxime was 33–48 per cent. This latter method was used to reduce 3,4-methylenedioxy-β-nitrostyrene to the desired aldoxime in 75 per cent yield and also was used successfully for the similar reduction of 3,4-dimethoxy-β-nitrostyrene (624). About this time two patents were issued to Bayer and Company, the first (58) describing the reduction of 3,4-methylenedioxy-β-nitrostyrene to 3,4-methylenedioxyphenylacetaldoxime by means of zinc and alcoholic acetic acid and to the aldoxime and 3,4-methylenedioxy-β-phenethylamine by means of aluminum and alcohol. The second patent (59) described the electrolytic reduction of the same nitro compound to the corresponding amine by means of a lead cathode in aqueous sulfuric and acetic acids.

Späth was the first investigator to reduce successfully the phenylacetaldoximes to the corresponding phenethylamines. Using sodium amalgam and alcoholic

acetic acid he converted 3,4,5-trimethoxyphenylacetaldoxime to 3,4,5-trimethoxyphenethylamine (698). The overall yield from the corresponding nitro-
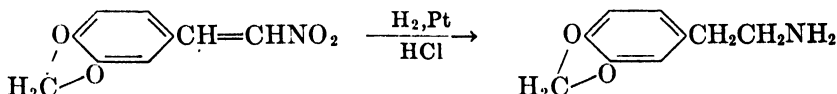
$$CH_3O\underset{CH_3O}{\overset{CH_3O}{\diamondsuit}}CH_2CH=NOH \quad \xrightarrow[C_2H_5OH,CH_3COOH]{Na-Hg} \quad$$

$$CH_3O\underset{CH_3O}{\overset{CH_3O}{\diamondsuit}}CH_2CH_2NH_2$$
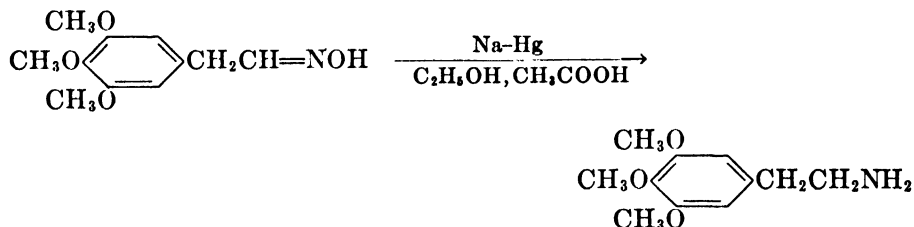
styrene was 25 per cent. Later Späth and Dobrowsky (699) obtained a 16 per cent yield of 3-methoxy-4-ethoxy-β-phenethylamine from 3-methoxy-4-ethoxy-β-nitrostyrene by utilizing the same technique.

The early attempts to reduce nitrostyrenes with hydrogen and a catalyst yielded dimeric products. Thus, in the presence of platinum black Sonn and Schellenberg (693) obtained from β-nitrostyrene two compounds in 19 and 44 per cent yields, respectively, which presumably are the stereoisomeric forms of 2,3-diphenyl-1,4-dinitrobutane.

$$2C_6H_5CH=CHNO_2 \quad \xrightarrow{(II)} \quad O_2NCH_2\overset{C_6H_5}{\underset{}{CH}}-\overset{C_6H_5}{\underset{}{CH}}CHCH_2NO_2$$
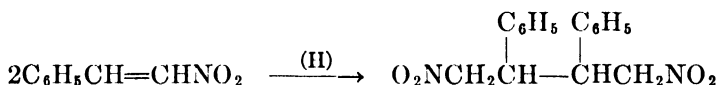
Two isomeric dimers also were obtained from 3,4-methylenedioxy-β-nitrostyrene. Using a mixture of ether and acetic acid instead of alcohol as the solvent, Banus and Vila (50) obtained low yields of both the diphenyldinitrobutane and phenylacetaldoxime from β-nitrostyrene. In either alcohol or ether Kohler and Drake (398) for the most part obtained the diphenyldinitrobutane, although the phenylacetaldoxime became the principal reaction product if hydrochloric acid was present. The same results were observed with a nickel catalyst. Skita (676) first reported the successful catalytic reduction of β-nitrostyrenes to β-phenethylamines. β-Phenethylamine and bis(β-phenethyl)amine were obtained from β-nitrostyrene and 3,4-methylenedioxy-β-phenethylamine from 3,4-methylenedioxy-β-nitrostyrene using a platinum catalyst, and p-methoxy-β-phenethylamine from p-methoxy-β-nitrostyrene using a palladium and then a platinum catalyst.

$$O\underset{H_2C}{\overset{/}{\diamondsuit}}\overset{}{O}CH=CHNO_2 \quad \xrightarrow[HCl]{H_2,Pt} \quad O\underset{H_2C}{\overset{/}{\diamondsuit}}\overset{}{O}CH_2CH_2NH_2$$

In all cases hydrochloric acid was included in the reaction mixture.

Of the three successful methods whose development has just been outlined—namely, catalytic reduction, electrolytic reduction, and reduction through the phenylacetaldoxime—the last mentioned has been the least used. It has the disadvantage of involving two steps and of giving low yields. Thus, Shoesmith and Connor (668) obtained a very small yield of m-methoxy-β-phenethylamine

from *m*-methoxy-β-nitrostyrene by this technique. Incidentally, De (157) was unsuccessful in subsequent attempts to reduce this particular nitrostyrene. Kobayashi (395) used this method to obtain 10 per cent of 3-methoxy-4-hydroxy-β-phenethylamine from either 3-methoxy-4-hydroxy-β-nitrostyrene or its acetate. The method was not effective for the reduction of 3-methoxy-4-methoxymethyleneoxy-β-nitrostyrene to the corresponding amine, and the reduction of 3-methoxy-4-benzyloxy-β-nitrostyrene proceeded only as far as the phenylacetaldoxime. Jansen (352, 353) obtained only 20 per cent of 2,4,5-trimethoxyphenylacetaldoxime by treating 2,4,5-trimethoxy-β-nitrostyrene with zinc and acetic acid. The amine was obtained by treatment with sodium amalgam. On the other hand Späth, Orechoff, and Kuffner (700) obtained 95 per cent of 3-benzyloxy-4-methoxyphenylacetaldoxime from 3-benzyloxy-4-methoxy-β-nitrostyrene.

$$CH_3O\langle\text{—}\rangle CH{=}CHNO_2 \quad \xrightarrow[CH_3COOH]{Zn}$$
$$C_6H_5CH_2O$$

$$CH_3O\langle\text{—}\rangle CH_2CH{=}NOH$$
$$C_6H_5CH_2O$$
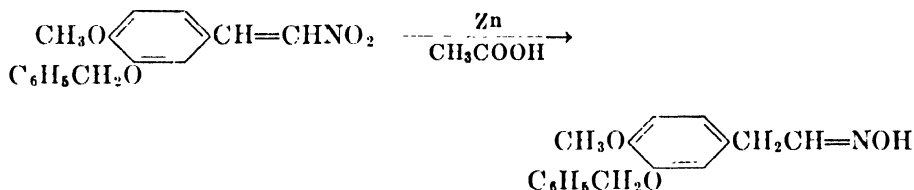
Probably the most widely used technique for reducing β-nitrostyrenes to β-phenethylamines is the electrolytic method. It achieved particularly extensive application for the seven years preceding the development of satisfactory catalytic techniques, but has not been employed as much since that time. The usual technique w... use a lead cathode and a mixture of alcohol, acetic acid, and hydrochloric acid as the electrolyte. In table 3 are listed the β-nitrostyrenes which have been reduced to β-phenethylamines by this method. Under the same conditions *m*,β-dinitrostyrene yielded 54 per cent of *m*-amino-β-phenethylamine, 4-methoxy-β,3-dinitrostyrene 47 per cent of 3-amino-4-methoxy-β-phenethylamine, and 4,5-dimethoxy-3,β-dinitrostyrene 49 per cent of 3-amino-4,5-dimethoxy-β-phenethylamine (684).

Subsequent to Skita's first description of the catalytic hydrogenation of β-nitrostyrene to ...-phenethylamine, Sawai (648) hydrogenated 3-methoxy-4-ethoxy-β-nitrosty... un... to 3-methoxy-4-ethoxy-β-phenethylamine with a platinum catalyst. Skita and Feil (677) reduced *p*-methoxy-β-nitrostyrene (16 per cent yield), 3,4-dimethoxy-β-nitrostyrene, and 3,4,5-trimethoxy-β-nitrostyrene (28 per cent yield) to the corresponding β-phenethylamines with hydrogen in the presence of a catalyst.

Kindler, Brandt, and Gehlhaar (380) were the first to effect this type of reduction in good yields. They used a palladium catalyst and dissolved their β-nitrostyrene in glacial acetic acid containing sulfuric acid. At 15°C. 90 per cent of the hydrogenation was complete in 2 min. and the reaction was over in 10 min. Their yield of β-phenethylamine was 84 per cent. In the absence of sulfuric acid, 90 per cent of the reaction was complete in 10 hr. and the yield of β-phenethylamine was only 8 per cent.

TABLE 3

Electrolytic reduction of β-nitrostyrenes

β-NITROSTYRENE	YIELD	REFERENCE
	per cent	
p-Methoxy.		(409)
3,4-Dimethoxy		(52, 406, 408)
2,5-Dimethoxy	51	(718)
2,3,4-Trimethoxy	87	(683)
2,4,5-Trimethoxy		(352, 353)
3,4,5-Trimethoxy	77	(683)
3-Methoxy-4-ethoxy.		(410)
3,4-Diethoxy.	60.5	(679)
2,3,4-Triethoxy	73	(683)
3,4,5-Triethoxy	78	(683)
3,4-Methylenedioxy	76	(729, 730)
3,4-Methylenedioxy.	67	(679)
3-Benzyloxy-4-methoxy	60	(622)
3-Methoxy-4-benzoxy.	40–60	(752)
m-Bromo.		(407)
3-Bromo-4-methoxy		(407)
3,4-Dimethoxy-5-bromo	42	(752)
m-Carbomethoxy.	52	(682)
p-Carbomethoxy	49	(682)
m-Carbethoxy	53.5	(682)
p-Carbethoxy.	46	(682)

TABLE 4

Catalytic hydrogenation of β-nitrostyrenes

β-NITROSTYRENE	YIELD	REFERENCE
	per cent	
p-Methoxy	77	(379)
3,4-Dimethoxy	61	(379)
3,4-Dimethoxy	23	(487)
3,4,5-Trimethoxy.	84	(279)
3,4,5-Trimethoxy.	62	(379)
3,4-Methylenedioxy	93	(649, 650)
3,4-Methylenedioxy.	76	(379)
3,4-Methylenedioxy.	70	(487)
3-Methoxy-4,5-methylenedioxy.	76	(379)
m-Nitro (to m-amino).	41	(649)
o-Hydroxy.	79	(280)
m-Hydroxy	72.5	(280)
p-Hydroxy	85	(280)
3-Hydroxy-4-methoxy.	68	(279)
3-Methoxy-4-hydroxy.	84.5	(280)
p-Acetoxy.	80	(280)

This technique immediately received wide application with both palladium and platinum catalysts. By means of this procedure the β-nitrostyrenes listed in table 4 were reduced to the corresponding β-phenethylamines.

Recently it has been shown that β-nitrostyrene may be reduced to β-phenethylamine in 60 per cent yield by means of lithium aluminum hydride (534a).

Meanwhile Reichert and Koch (609) discovered that hydrogenation in pyridine solution gave the corresponding phenylacetaldoxime in excellent yield. They used a palladium catalyst on a charcoal carrier. The following β-nitrostyrenes were reduced by this technique: o-methoxy- (90 per cent) (607, 609), p-methoxy- (almost quantitative) (609), 2,4-dimethoxy- (92 per cent) (607, 609), 3,4-dimethoxy- (609), and 3,4,5-trimethoxy- (90 per cent) (606, 607). Several of these phenylacetaldoximes subsequently were reduced to the corresponding β-phenethylamines by means of hydrogen in the presence of a platinum catalyst. Alcohol was used as the solvent and oxalic acid was added to the reaction mixture. The yields were as follows: o-methoxy- (60 per cent) (607), 2,4-dimethoxy- (60 per cent) (607), and 3,4,5-trimethoxy- (80 per cent) (606, 607).

With a variety of reducing agents o,β-dinitrostyrene gave low yields of indole.
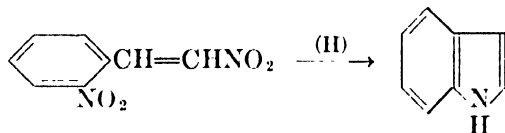
The results are as follows: iron and acetic acid, 9.4 per cent (440), 32 per cent (532); zinc and acetic acid, 11 per cent (440), low (532); and aluminum amalgam, some (440), trace (532). Alkaline sodium hydrosulfite yielded indigo (532).
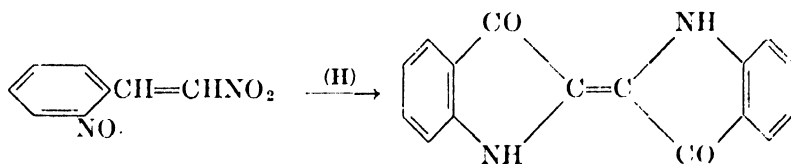
No tribromoindole was obtained when β,2-dinitro-3,4,5-tribromostyrene was treated with iron and acetic acid. However, with more active 2,β-dinitrostyrenes the method appears to have considerable synthetic utility. Thus, 4-acetoxyindole (29–35 per cent) (59a), 5-acetoxyindole (50–55 per cent) (59a), and 5,6-methylenedioxyindole (81 per cent) (131a) have been prepared in this way.

It is to be noted that all reductions of β-nitrostyrenes to β-phenethylamines which were effected in good yield were conducted in the presence of a strong acid. In the absence of such acid the reduction proceeded only as far as the phenylacetaldoxime. Kindler, Brandt, and Gehlhaar (380) postulated that in the presence of sulfuric acid they were actually reducing a molecular compound of the β-nitrostyrene and the acid.

$$C_6H_5CH{=}CHN\overset{\nearrow O}{\underset{\searrow O\text{----}HSO_4H}{}}$$
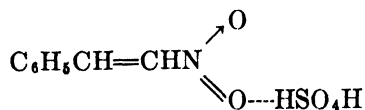
The effect of the acid was to polarize the molecule by drawing the electrons away from the benzene ring. This concentrated the unsaturation at the far end of the chain (on the carbon atom attached to the ring) and thereby facilitated reduction at this point. It particularly avoided the formation of radicals of the type

$$C_6H_5\underset{|}{C}HCH_2NO_2$$

which could dimerize to give the bimolecular reduction products described by Sonn and Schellenberg (693). Apparently the general effect of a strong acid is just this type of polarization which weakens the double bonds and facilitates the addition of hydrogen. It is equally applicable to the β-nitrostyrenes or the phenylacetaldoximes. In the absence of such polarization the oxime is stable to further reduction under most of the conditions which have been tried. In pyridine solution particularly high yields of the oxime have been obtained. It would be expected that pyridine would form a loose molecular complex with the oxime

$$C_6H_5CH_2CH{=}NOH{\leftarrow}NC_5H_5$$

which would give the reverse polarization from that produced by a strong acid and therefore would increase the difficulty of further reduction.

II. OXIDATION

A. Oxidation to aromatic acids

The first application of oxidation in the field of styrene chemistry was in structure proof where the side chain was oxidized to a carboxyl group. Location of the side chain by this means subsequently has been utilized very often.

In 1844 Kopp first oxidized styrene to benzoic acid by means of chromic acid (411). With boiling concentrated nitric acid the product was nitrobenzoic acid.

$$C_6H_5CH{=}CH_2 \xrightarrow{CrO_3} C_6H_5COOH$$
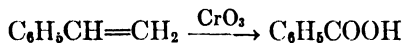
Blyth and Hofmann (87) also obtained nitrobenzoic acid when they oxidized styrene with nitric acid. Benzoic acid and benzaldehyde were obtained as by-products. With potassium dichromate and sulfuric acid benzoic acid was produced. Oxidation to benzoic acid was one means utilized by Dykstra to identify styrene (181). With nitric acid and bromine styrene yielded a mixture of bromonitromethanes (154).

In table 5 are summarized the oxidations of some substituted styrenes to the corresponding aromatic acids. However, when the p-hydroxyl group in 3,4-

dimethoxystyrene was not etherified, dilute nitric acid removed the side chain, so that the product of the oxidation was methoxyquinone (249).

$$HO\text{—}\langle\text{—}\rangle\text{—}CH{=}CH_2 \quad \xrightarrow{HNO_3} \quad O{=}\langle\text{—}\rangle{=}O$$
$$CH_3O \qquad\qquad\qquad\qquad CH_3O$$
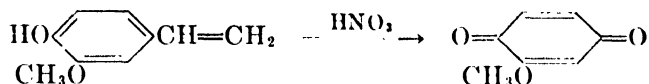
Styrenes with halogen in the β-position in the side chain are oxidized with greater difficulty than unsubstituted styrenes. Thus, β-bromostyrene is oxidized

TABLE 5

Oxidation of styrenes to aromatic acids

STYRENE	OXIDIZING AGENT	BENZOIC ACID PRODUCED	REFERENCE
p-Methyl ..	HNO₃	p-Methyl	(215)
2,4-Dimethyl	KMnO₄	2,4-Dimethyl	(483)
3,4-Dimethyl .	KMnO₄	3,4-Dimethyl	(483)
tert-Butyl	Cold CrO₃	(No oxidation)	(551)
p-Methoxy	KMnO₄	p-Methoxy	(581)
2-Methyl-4-methoxy	KMnO₄	2-Methyl-4-methoxy	(582)
3-Methyl-4-methoxy .	KMnO₄	3-Methyl-4-methoxy	(582)
5-Methyl-2-methoxy..	KMnO₄	5-Methyl-2-methoxy	(582)
2-Methyl-4-methoxy-5-isopropyl . .	KMnO₄	2-Methyl-4-methoxy-5-isopropyl	(582)
2,6-Dimethoxy	KMnO₄	2,6-Dimethoxy	(667)
3-Nitro-4-methoxy. .	KMnO₄	3-Nitro-4-methoxy	(184)
2,4-Dimethoxy ..	KMnO₄	2,4-Dimethoxy	(223)
	HNO₃	2,4-Dimethoxy	(223)
3,4-Dimethoxy	KMnO₄	3,4-Dimethoxy	(249)
	HNO₃	3,4-Dimethoxy	(249)
p-Dimethylamino	KMnO₄	(Not isolated)	(111)
o-Dimethylamino methyl	KMnO₄	(Not isolated)	(188)
o-(β-Dimethylaminoethyl)	KMnO₄	(Not isolated)	(116)
β-(N-Methyl)-3,4-diacetoxy	KMnO₄	(Not isolated)	(118)
p-N,N-Dimethylsulfonamido	KMnO₄	p-N,N-Dimethylsulfonamido	(349)

with difficulty by potassium permanganate (303), since it is more resistant than unsaturated aliphatic bromides to this reagent. Similarly chromic and sulfuric acids at 95°C. did not affect β-chlorostyrene and while some benzoic and formic acids were obtained from β-bromostyrene, 60 per cent of the styrene was recovered unchanged (147). β-Chlorostyrene was oxidized to benzoic acid by potassium dichromate and nitric acid (269). In table 6 are summarized the oxidations of some other halogenated and nitrated styrenes to the corresponding aromatic acids.

Treatment of what was probably 3-carboxy-4-methoxy-β,β-dichlorostyrene with fuming nitric acid at 100°C. yielded 4-methoxyisophthalic acid (321). Both β,β-dichlorostyrene and α,β,β-trichlorostyrene gave a mixture of benzoic and p-nitrobenzoic acids when treated with nitrogen tetroxide at 100°C. (86).

With methylated nitrostyrenes potassium permanganate has given variable results. Thus, Worrall has used it to oxidize 4-methyl-β,3-dinitrostyrene to 3-nitro-4-methylbenzoic acid (790). On the other hand, Hanzlik and Bianchi

TABLE 6

Oxidation of halogenated and nitrated styrenes

STYRENE	OXIDIZING AGENT	PRODUCT OBTAINED	REFERENCE
2-Bromo-4-trifluoromethyl..	KMnO₄	2-Bromo-4-trifluoro-methylbenzoic acid	(43)
α,β-Dibromo.	KMnO₄	Benzoic acid	(17)
β,p-Dibromo..	KMnO₄	p-Bromobenzoic acid	(614)
2-Methoxy-β,3,5-tribromo..	KMnO₄	2-Methoxy-3,5-dibromobenzoic acid	(248)
3-Methoxy-β,6-dibromo...	KMnO₄	(Not isolated)	(612)
p-Methoxy-β-chloro.....	KMnO₄	Anisic acid	(583)
p-Methoxy-α-chloro....	KMnO₄	Anisic acid	(583)
4-Methyl-β,2-dichloro..	KMnO₄	2-Chloro-4-methylbenzoic acid	(32)
2,4-Dimethyl-β-chloro..	KMnO₄	2,4-Dimethylbenzaldehyde	(42)
2,4-Dimethyl-β,6-dichloro ..	KMnO₄	2,4-Dimethyl-6-chlorobenzaldehyde	(42)
β-Nitro	K₂Cr₂O₇ + H₂SO₄	Benzoic acid	(571)
β,o-Dinitro.. ..	KMnO₄	o-Nitrobenzoic acid	(571)
β,p-Dinitro....	CrO₃	p-Nitrobenzoic acid	(571)
β-Chloro-β,p-dinitro....	CrO₃ + CH₃COOH	p-Nitrobenzoic acid	(560)
4-Methoxy-β,3-dinitro..	KMnO₄	3-Nitroanisic acid	(184)
2-Bromo-β,5-dinitro...	KMnO₄	2-Bromo-5-nitrobenzoic acid	(794)
2-Iodo-β,5-dinitro..........	KMnO₄	2-Iodo-5-nitrobenzoic acid	(793)

(284) obtained nitroterephthalic acid from 4-methyl-β,3-dinitrostyrene using permanganate but got 3-nitro-4-methylbenzoic acid using nitric acid. Franzen and Schneider (235) obtained 4-nitrophthalic acid by treating 2-methyl-β,4-dinitrostyrene with potassium permanganate.
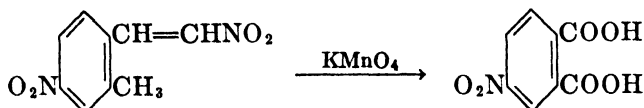
B. Ozonization

The first ozonization of styrene itself was reported in 1930, by Brus and Peyresblanques (127), who showed that ozone was absorbed quantitatively by

the side chain before the nucleus was attacked. Briner and Gelbert (122) ozonized styrene in carbon tetrachloride solution. Decomposition of the ozonide with hot water yielded benzaldehyde and formic acid. When allowed to stand for 10 hr., styrene ozonide slowly evolved a gas which consisted of 40 per cent hydrogen, 45 per cent carbon dioxide, and 15 per cent methane. Benzoic acid was isolated from the non-volatile residue. Styrene ozonide was too unstable to permit the measurement of the heat of ozonization of styrene (123). Since Marvel and Nichols (481) isolated dibenzaldehyde peroxide (I) from the ozonization of styrene even under strictly anhydrous conditions, they postulated that styrene ozonide decomposed directly to the ozonization products without ever passing

TABLE 7

Molecular weight of styrene ozonide

SOLVENT	$(C_8H_8O_3)_4$	$(C_8H_8O_3)_4$	$(C_8H_8O_3)_2$
	per cent	per cent	per cent
CCl_4	56	33	
C_6H_6	59	29	
$CHCl_3$		57	35
$(C_2H_5)_2O$			74

through an intermediate dihydroxydibenzaldehyde peroxide (II) whose presence they were never able to detect.
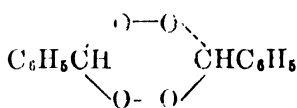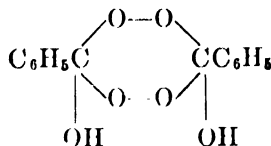
I   II

Kawamura (366) obtained benzaldehyde, formaldehyde, and hydrogen peroxide by decomposing styrene ozonide with hot water. He reported the ozonide to be largely polymeric, with the molecular weight depending on the solvent used. These results are summarized in table 7.

Semmler (665) was the first to use ozonization for structure proof in the styrene series. β-Acetoxystyrene was oxidized to a mixture of benzaldehyde and benzoic acid by this method. Subsequently a number of styrenes were ozonized and the corresponding benzaldehydes isolated in each case. These include a mixture of o- and p-methoxystyrenes (581), β-chloro-p-methoxystyrene (583), α-chloro-p-methoxystyrene (583), 3-hydroxy-4-ethoxystyrene (359), 2-methoxy-5-isopropylstyrene (585), and 3-methoxy-4-hydroxystyrene (62–74 per cent yield) (652).

C. Air oxidation

Moureu and Dufraisse (523), who were the first to investigate this reaction, found that the following substances were positive catalysts for the air oxidation

of styrene: I_2, KI, NaI, LiI, MgI_2, ZnI_2, FeI_2, NH_4I, $CH_3NH_2 \cdot HI$, $(CH_3)_2NH \cdot HI$, $(CH_3)_3N \cdot HI$, CHI_3. This effect was investigated further (524) and the following compounds added to the list: Sb_2O_5, SbI_3, $SbBr_3$, $SbCl_3$, $(C_6H_5)_2SbCl$, $(C_6H_5)_3SbCl_2$, $Bi(NO_3)_3$, $BiBr_3$, BiI_3, $(C_2H_5)_3Bi$, $(C_3H_7)_3Bi$, V_2O_3, V_2O_5, $VOCl_3$, NH_4VO_3. The following substances inhibited the air oxidation of styrene: tartar emetic, $(C_6H_5)_3Sb$, Bi, Bi_2O_3, $[(CH_3)_2CH(CH_2)_2]_3Bi$, $(C_6H_5)_3Bi$. Triphenylmethyl also is a catalyst for the air oxidation of styrene (806).

Styrene is a fairly strong inhibitor for the oxidation of benzaldehyde in the presence of light (594). In this case styrene oxide was isolated after blowing a mixture of benzaldehyde and styrene with oxygen. A careful study of the oxidation and polymerization of styrene at 70-90°C. in the presence of benzaldehyde, formaldehyde, polystyrene, or benzoyl peroxide showed that the oxidation of styrene consists of two chain reactions involving peroxides and propagated through free radicals (489). The direct oxidation of styrene with air over a nickel–chromium gauze catalyst at 110°C. yielded formaldehyde as one of the products (539).

The oxidation of an α-halostyrene with oxygen is particularly interesting in that it leads directly to the corresponding benzoyl halide and formaldehyde.

$$C_6H_5CCl{=}CH_2 + O_2 \rightarrow C_6H_5COCl + HCHO$$
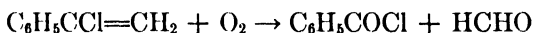
These products have been isolated in the case of α-chlorostyrene (174). In the case of p-methoxy-α-chlorostyrene it was shown that the anisic acid which was isolated came from anisoyl chloride (583). For the air oxidation of α-bromostyrene, sodium iodide and methylammonium iodide have been shown to be positive catalysts, while iodine, ferrous iodide, and iodoform are negative (523).

D. Epoxidation

Böeseken and Derx (93) originally showed that styrene formed an epoxide on treatment with perbenzoic acid more easily than did 1,4-dihydronaphthalene,

$$C_6H_5CH{=}CH_2 + C_6H_5CO_3H \rightarrow C_6H_5CH\underset{O}{\overset{\diagup\!\!\!\diagdown}{\quad}}CH_2 + C_6H_5COOH$$
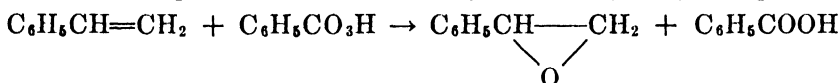
indene, or 1,2-dihydronaphthalene. Hibbert and Burt obtained 70–75 per cent yields of styrene oxide by conducting this oxidation in chloroform at 0°C. (297, 298). Golumbic and Cottle (273) found their product to be contaminated with a little phenylacetaldehyde. The epoxidation also can be effected with peracetic acid (728); in this case the reaction has been shown to be bimolecular as a result of rate studies made with a number of olefins (97, 716).

E. Miscellaneous oxidations

When styrene was treated with hydrogen peroxide at 0°C. in tert-butyl alcohol solution in the presence of osmium tetroxide, the product was a 50 per cent yield of styrene glycol (511). Treatment of styrene with potassium permanganate in

$$C_6H_5CH{=}CH_2 + H_2O_2 \xrightarrow{\quad OsO_4 \quad} C_6H_5CHOHCH_2OH$$
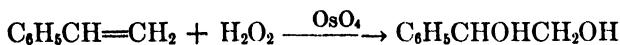
the presence of very dilute sodium hydroxide produced a 69 per cent crude yield (55 per cent pure) of phenylglyoxylic acid, together with a 7 per cent yield of benzoic acid (320). Styrene and chromyl chloride reacted to form an addition

$$C_6H_5CH{=}CH_2 \cdot \xrightarrow[\text{aqueous NaOH}]{\text{KMnO}_4} C_6H_5COCOOH + C_6H_5COOH$$
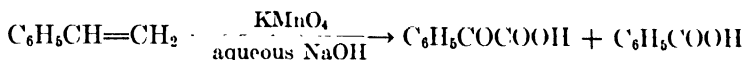
compound which decomposed on treatment with water to give benzaldehyde, chlorinated products, and a trace of phenylacetaldehyde (290). Styrene did not react with selenium dioxide at 140°C. and yielded complex products at higher temperatures (620). It has been reported that when styrene and oxygen are passed over active carbon at 100–110°C. very small amounts of pentoses are produced (538). Oxidation of 3-methoxy-4-acetoxystyrene with sodium dichromate and sulfuric acid at 50°C. yielded 71 per cent of vanillin (652).

III. CHLORINATED DERIVATIVES

A. Addition of chlorine

Laurent (435) in 1844 was the first to add chlorine to styrene. He also described

$$C_6H_5CH{=}CH_2 + Cl_2 \rightarrow C_6H_5CHClCH_2Cl$$
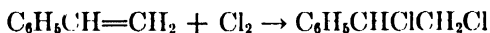
a chlorinated styrene where one hydrogen atom was replaced by chlorine (probably α-chlorostyrene). It was obtained by treating styrene dichloride with potassium hydroxide. A derivative also was mentioned from which two hydrogen atoms were lost and to which eight chlorine atoms were added. Blyth and Hofmann (87) also added chlorine to styrene and mentioned that the resulting styrene dichloride lost hydrogen chloride on treatment with alcoholic potassium hydroxide. Berthelot (72, 77) mentions the addition of chlorine as one of the characteristic reactions of styrene. Biltz (85) found chloroform to be a suitable solvent for this addition. In carbon tetrachloride solution with no particular precautions for the exclusion of light, the product was about three parts of styrene dichloride to one of β-chlorostyrene (197).

Styrene dichloride has been obtained in several other ways. It constitutes 10 per cent of the product when styrene is treated with bromine chloride (759). It is obtained in 50 per cent yield, along with 36 per cent of β-styrenephosphonic acid, when styrene is treated with phosphorus trichloride and chlorine in anhydrous benzene (412). It is one of the products of the reaction between styrene

$$C_6H_5CH{=}CH_2 \xrightarrow[\text{C}_6\text{H}_6]{\text{PCl}_3 + Cl_2} C_6H_5CHClCH_2Cl + C_6H_5CH{=}CHPO_3H_2$$
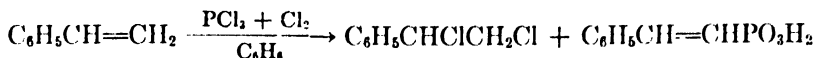
and nitrosyl chloride (555) and also is formed by the chlorination of ethylbenzene at its boiling point. In this latter reaction Evans, Mabbot, and Turner (213) have postulated its formation as the addition of chlorine to styrene formed by dehydrochlorination of chloroethylbenzene in the mixture. Styrene dichloride

$$C_6H_5C_2H_5 \xrightarrow{Cl_2} C_6H_5C_2H_4Cl \xrightarrow{-HCl} C_6H_5CH{=}CH_2 \xrightarrow{Cl_2} C_6H_5CHClCH_2Cl$$
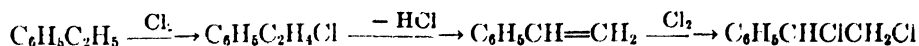
has been postulated as the initial product of the reaction between benzene and s-dichloroethylene in the presence of an aluminum–mercury couple (91). The styrene dichloride reacts further with another molecule of benzene to give as the final product 2-chloro-1,1-diphenylethane.

$$C_6H_6 + CHCl{=}CHCl \xrightarrow{AlCl_3} [C_6H_5CHClCH_2Cl] \xrightarrow{C_6H_6} (C_6H_5)_2CHCH_2Cl$$

3,4-Methylenedioxystyrene readily yields the dichloride when treated with chlorine in carbon tetrachloride solution (51 (72 per cent yield), 100, 495, 496). p-Methoxystyrene dichloride has been prepared in 25–30 per cent yield by treating anisole with chloroacetal and hydrogen chloride at 60–70°C. (583). With o-cresyl methyl ether, p-cresyl methyl ether, and thymol methyl ether the yields

$$C_6H_5OCH_3 + ClCH_2CH(OC_2H_5)_2 \xrightarrow{HCl} CH_3O\langle\underline{\quad}\rangle CHClCH_2Cl$$
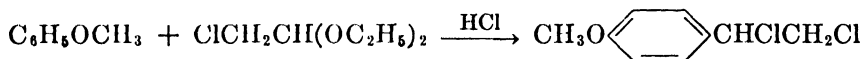
fell to 5 per cent. In the case of thymol two other compounds were isolated from the reaction mixture.
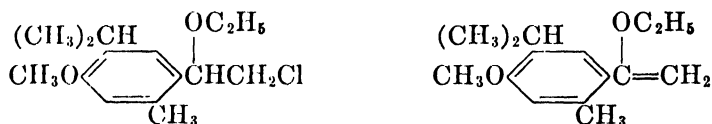
These products suggest that the reaction with β-chloroacetal involves the active p-hydrogen and the α,β-dichloro ether:
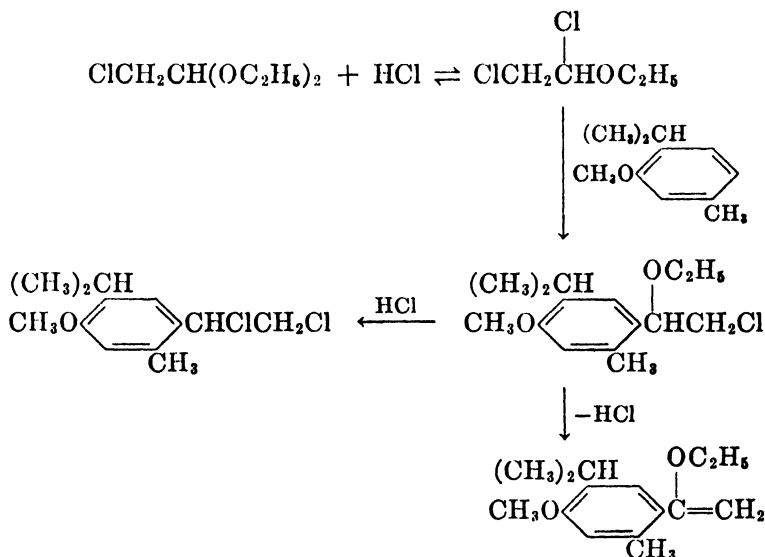
All four of these dichlorides (p-methoxystyrene dichloride, 3-methyl-4-methoxy-styrene dichloride, 2-methoxy-5-methylstyrene dichloride, and 2-methyl-4-methoxy-5-isopropylstyrene dichloride) were prepared in 25 per cent yield by treating the corresponding styrene with chlorine.

Priebs (571) found that β-nitrostyrene readily added chlorine in chloroform solution. Pfeiffer (560) found the same to be true of β,p-dinitrostyrene (53 per

$$O_2N\langle\rangle CH{=}CHNO_2 \xrightarrow{Cl_2} O_2N\langle\rangle CHClCHClNO_2$$
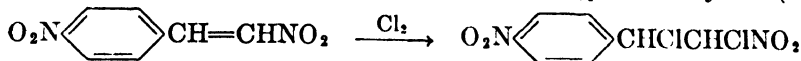
cent yield), and Worrall and Finkel (794) extended the reaction to β,5-dinitro-2-bromostyrene.

When styrene dichloride was heated for several hours at 120°C. with aqueous

$$C_6H_5CHClCH_2Cl \xrightarrow[CaCO_3]{H_2O} C_6H_5CHOHCH_2Cl + C_6H_5CHOHCH_2OH$$
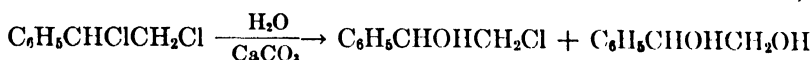
calcium carbonate, there was obtained a 70 per cent yield of styrene chlorohydrin
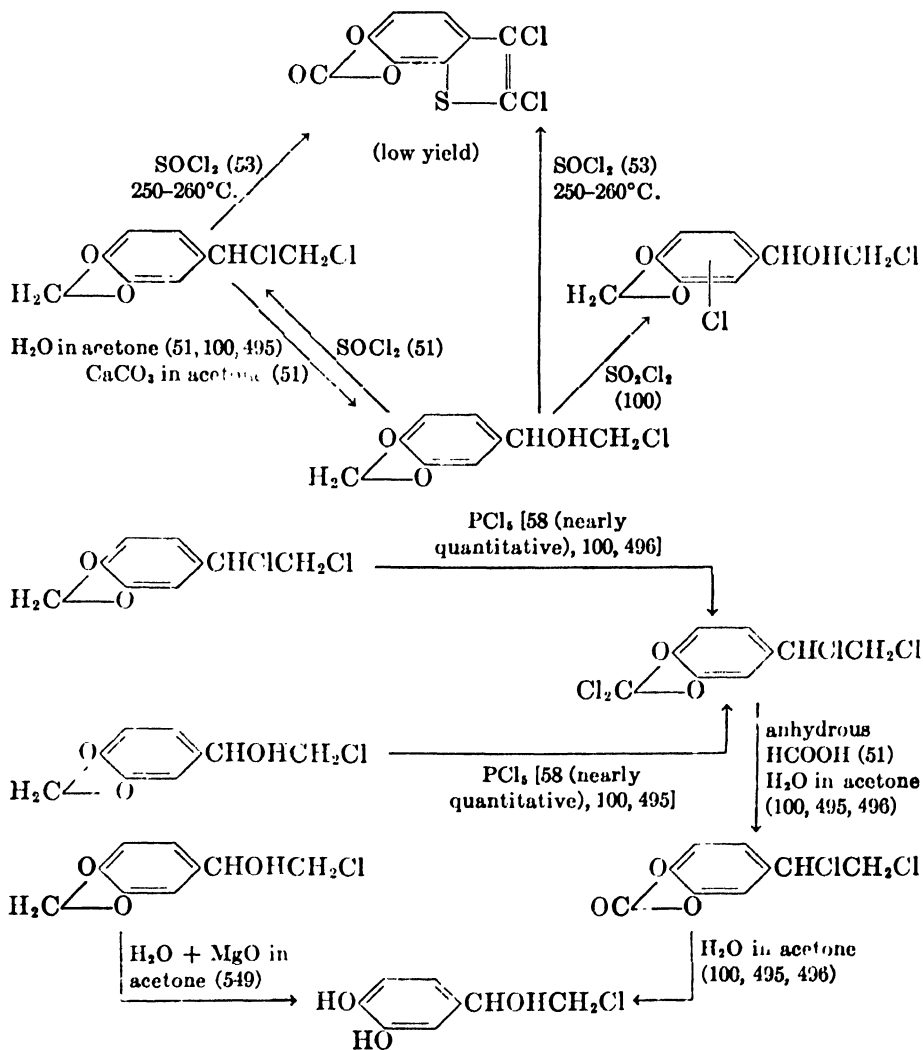
contaminated with a trace of styrene glycol (330). With sodium acetate the yield was 70–80 per cent, with sodium carbonate 40 per cent, and with calcium hydroxide "good."

In the case of the last-named reagent styrene glycol was obtained exclusively if one mole of calcium hydroxide was used instead of the one-half mole necessary for chlorohydrin formation. When this type of hydrolysis was utilized as an analytical procedure (647), the styrene dichloride was boiled with potassium hydroxide in benzyl alcohol, cooled, diluted with water, and the liberated halide titrated with silver nitrate.

The conversion of 3,4-methylenedioxystyrene dichloride to the corresponding chlorohydrin has been examined as a route to 3,4-dihydroxystyrene chlorohydrin. The various transformations studied are shown in the chart on page 201.

When styrene dichloride was distilled from pyridine, a 90 per cent yield of β-chlorostyrene was obtained (329). This reaction also has been employed for

$$C_6H_5CHClCH_2Cl \xrightarrow{\text{pyridine}} C_6H_5CH{=}CHCl$$

(90 per cent)
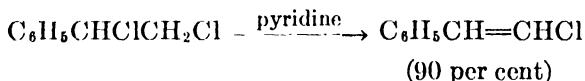
the preparation of p-methoxy-β-chlorostyrene, 3-methyl-4-methoxy-β-chlorostyrene, 2-methoxy-5-methyl-β-chlorostyrene, and 2-methyl-4-methoxy-5-isopropyl-β-chlorostyrene from the corresponding substituted styrene dichlorides (583). A yield of 92 per cent of β-chlorostyrene has been obtained by passing styrene dichloride vapors together with steam over alumina at 360–400°C. (197).

On the other hand, treatment of styrene dichloride with alcoholic sodium hydroxide yielded 89 per cent of α-chlorostyrene (197). As mentioned previously, this reaction had been observed by the earliest investigators (87, 435). Glaser

$$C_6H_5CHClCH_2Cl \xrightarrow[C_2H_5OH]{NaOH} C_6H_5CCl{=}CH_2$$

(89 per cent)
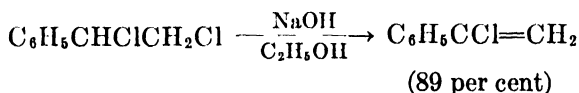
(269) obtained α-chlorostyrene by boiling styrene dichloride with calcium oxide. Alcoholic sodium ethoxide has been used similarly to prepare p-methoxy-α-chlorostyrene, 3-methyl-4-methoxy-α-chlorostyrene, 2-methoxy-5-methyl-α-chlorostyrene, and 2-methyl-4-methoxy-5-isopropyl-α-chlorostyrene from the corresponding substituted styrene dichlorides (583). When p-methoxystyrene dichloride was treated with potassium hydroxide in aqueous ethanol, both p-methoxy-α-chlorostyrene and p-methoxy-α-ethoxy-β-chloroethylbenzene were obtained. The latter compound was the sole product obtained by treating p-methoxystyrene dichloride with alcoholic potassium cyanide.
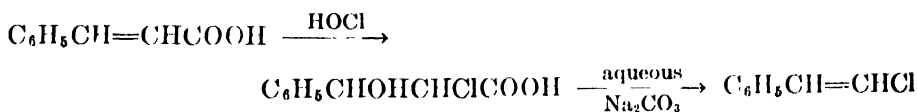
$$CH_3O\!\!\left\langle\underline{}\right\rangle\!\!CHClCH_2Cl \xrightarrow[C_2H_5OH]{KOH,\ H_2O}$$

$$CH_3O\!\!\left\langle\underline{}\right\rangle\!\!CCl{=}CH_2 \ + \ CH_3O\!\!\left\langle\underline{}\right\rangle\!\!\underset{\underset{OC_2H_5}{|}}{CHCH_2Cl}$$
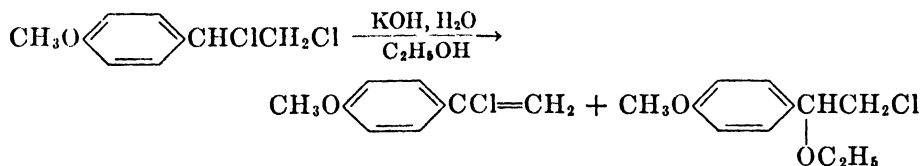
Priebs (571) reported that treatment of β-nitrostyrene dichloride with dilute sodium hydroxide yielded α-chloro-β-nitrostyrene. Subsequent investigators have always obtained the β-halostyrene in this type of reaction. Since Thiele and Haeckel (737) showed Priebs to be wrong in the case of the bromo compound, his formulation here probably was incorrect also. Thus Pfeiffer (560) obtained β-chloro-β,p-dinitrostyrene by treating β,p-dinitrostyrene dichloride with aqueous sodium hydroxide, and Worrall and Finkel (794) obtained β-chloro-2-

$$O_2N\langle\rangle CHClCHClNO_2 \xrightarrow[H_2O]{NaOH} O_2N\langle\rangle CH\!=\!CClNO_2$$
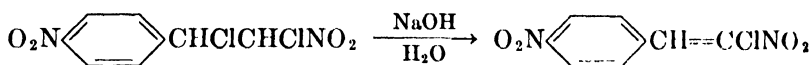
bromo-β,5-dinitrostyrene by treating 2-bromo-β,5-dinitrostyrene dichloride with alcoholic potassium acetate. Similarly, p-methyl-β-nitrostyrene dichloride yielded p-methyl β-chloro-β-nitrostyrene (790).

B. β-Chlorostyrene chemistry

The preparation of β-chlorostyrenes from styrene dichlorides has been described above. While a very convenient method, it has not been as widely used as the various routes from cinnamic acid. In 1845 Stenhouse (708, 709) first obtained a chlorine-containing oil by treating cinnamic acid with bleaching powder, potassium hypochlorite, or chlorine and hot water. In 1864 Erlenmeyer (201) showed that it had the empirical formula C_8H_7Cl. Glaser (269) added hypochlorous acid to cinnamic acid and then boiled the adduct with aqueous sodium carbonate. He placed the chlorine in the product in the α-position. Erlenmeyer (204) later showed Glaser's compound to be β-chlorostyrene, since it did not have the same properties as the α-chlorostyrene which Friedel obtained by treating acetophenone with phosphorus pentachloride followed by potassium hydroxide.

$$C_6H_5CH\!=\!CHCOOH \xrightarrow{HOCl}$$

$$C_6H_5CHOHCHClCOOH \xrightarrow[Na_2CO_3]{aqueous} C_6H_5CH\!=\!CHCl$$

$$C_6H_5COCH_3 \xrightarrow{PCl_5} C_6H_5CCl_2CH_3 \xrightarrow{KOH} C_6H_5CCl\!=\!CH_2$$

Erlenmeyer (207) obtained a 97 per cent yield of β-chlorostyrene by treating cinnamic acid dichloride with cold aqueous sodium carbonate.

$$C_6H_5CHClCHClCOOH \xrightarrow[Na_2CO_3]{aqueous} C_6H_5CH\!=\!CHCl$$
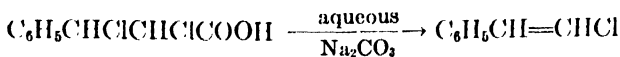
Biltz (85, 449) used hot carbonate and v. Auwers (34) found cold or hot carbonate equally useful. Durrans (178) used aqueous sodium hydroxide to decompose his cinnamic acid dichloride, while Dann, Howard and Davies (150) used aqueous sodium acetate (60 per cent yield). This alkaline decomposition of a cinnamic acid dichloride has been found equally suitable for the preparation of p-methyl-β-chlorostyrene (40), o-iodo-β-chlorostyrene (774), and β,p-dinitro-β-chlorostyrene (560).

When Read and Andrews treated cinnamic acid with cold dilute chlorine water a 91 per cent yield of α-chloro-β-hydroxycinnamic acid was obtained

$$C_6H_5CH\!\!=\!\!CHCOOH \xrightarrow[\text{H}_2\text{O}]{\text{Cl}_2} C_6H_5CHOHCHClCOOH$$
$$+ \; C_6H_5CHClCHClCOOH + C_6H_5CH\!\!=\!\!CHCl$$
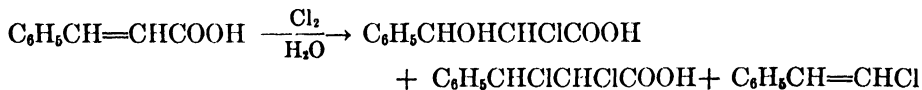
(596). By-products included 1 per cent of cinnamic acid dichloride and 8 per cent of β-chlorostyrene. The same reaction has been observed by other investigators (94), who have isolated such other by-products as phenylacetaldehyde (210) and α-hydroxy-β,β-dichloroethylbenzene (228). In the latter case the yield of α-chloro-β-hydroxycinnamic acid was 73.5 per cent, of β-chlorostyrene 1.8 per cent, and of α-hydroxy-β,β-dichloroethylbenzene 16 per cent. When cold sodium hypochlorite was used in place of cold chlorine water the yield of acid was 72

TABLE 8

β-Chlorostyrenes from alkali cinnamates

ALKALI CINNAMATE	YIELD OF β-CHLOROSTYRENE OBTAINED	REFERENCE
	per cent	
p-Methoxy.	57	(99)
3,4-Methylenedioxy.	60	(99)
		(453)
o-Nitro..	16	(404, 405)
	5–15	(150)
m-Nitro.	5–15	(150)
p-Nitro ..	5–15	(150)

per cent and of β-chlorostyrene 28 per cent. It is interesting to note that the decomposition of α-chloro-β-hydroxycinnamic acid yielded mostly phenylacetaldehyde plus a little β-chlorostyrene (40).

$$C_6H_5CHOHCHClCOOH \rightarrow C_6H_5CH_2CHO + C_6H_5CH\!\!=\!\!CHCl$$

Recently it has been reported that treatment of sodium cinnamate with sodium hypochlorite and alcohol yielded chloroform, benzoic acid, and chlorostyrene (719). No chlorostyrene was obtained in the absence of alcohol.

With sodium p-nitrocinnamate and hypochlorous acid, not only was α-hydroxy-β-chloro-p-nitrophenylpropionic acid isolated, but also epoxy p-nitrocinnamic acid and p-nitro-β-chlorostyrene (207). With other substituted alkali cinnamates hypochlorous acid or sodium hypochlorite gave the β-chlorostyrene as the principal product of the reaction, as shown in table 8. In the case of sodium o-methoxycinnamate both mono- and di-chlorinated derivatives of o-methoxystyrene were obtained (552).

This same reaction was responsible for the by-product in another degradation. Treatment of styryl methyl ketone with sodium hypochlorite yielded besides

65–71 per cent of the expected cinnamic acid a small amount of β-chlorostyrene (669).

$$C_6H_5CH{=}CHCOCH_3 \xrightarrow{\text{NaOCl}} C_6H_5CH{=}CHCOOH + C_6H_5CH{=}CHCl$$
$$\text{(65–71 per cent)}$$
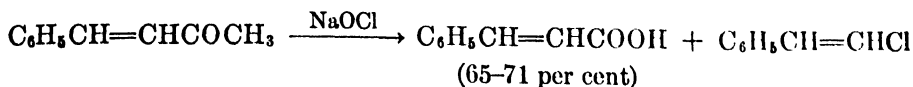
A related reaction is the nitration of α-chlorocinnamic acid with fuming nitric acid (560). At $-10°C$. there was obtained 62 per cent of p-nitro-α-chlorocinnamic acid together with a 6–12 per cent yield of β,p-dinitro-β-chlorostyrene. At

$$\text{(62 per cent)} \qquad\qquad \text{(6–12 per cent)}$$
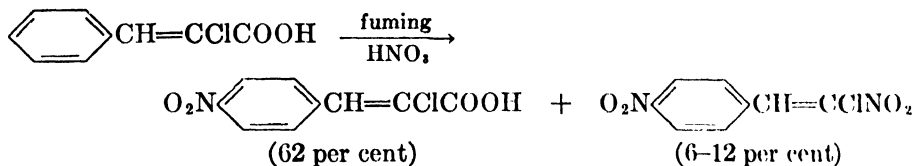
20–25°C. the yield of the styrene rose to 28 per cent, while the yield of nitro acid fell to 8 per cent.

Forrer (227) showed that β,β-dichloroethylbenzene, from phenylacetaldehyde and phosphorus pentachloride, gradually lost hydrogen chloride on standing. With alcoholic potassium hydroxide at 120°C. the product was β-chlorostyrene.

$$C_6H_5CH_2CHO \xrightarrow{\text{PCl}_5} C_6H_5CH_2CHCl_2 \xrightarrow{\text{KOH}} C_6H_5CH{=}CHCl$$

However, β,β-dichloroethylbenzene is less reactive toward potassium hydroxide than is α,α-dichloroethylbenzene (558). v. Auwers used this reaction to prepare a number of substituted β-chlorostyrenes. These included p-methyl- (37, 40), 2,4-dimethyl- (41), 3,4-dimethyl- (41), 2,4,5-trimethyl- (41), 2-chloro-4-methyl- (32), and 2,4-dimethyl-6-chloro- (32). He also prepared 2,4-dimethyl-β-chlorostyrene by the simultaneous decarboxylation and dehydrochlorination of α-dichloromethyl-2,4-dimethylphenylacetic acid with aqueous sodium carbonate (42).
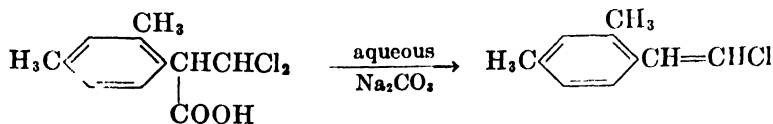
It also has been reported (666) that 2-methyl-4-methoxy-5-carboxy-β-chlorostyrene can be prepared by heating 2-methyl-4-methoxy-5-carboxy-β,β-dichloroethylbenzene with sodium hydroxide or by heating 2-methyl-4-hydroxy-5-carboxy-β,β-dichloroethylbenzene with methyl sulfate and sodium hydroxide.

When styrene chlorohydrin vapors, together with steam, were passed over a phosphoric acid on silica gel catalyst held at 370–400°C., a 63 per cent yield of β-chlorostyrene was obtained (197).

$$C_6H_5CHOHCH_2Cl \xrightarrow[\text{370–400°C.}]{\text{H}_2\text{O, HPO}_3, \text{SiO}_2} C_6H_5CH{=}CHCl$$
$$\text{(63 per cent)}$$
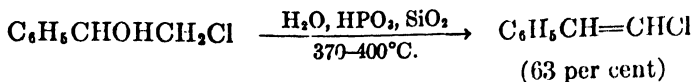
3,4-Methylenedioxy-β-chlorostyrene also has been prepared merely by heating the corresponding chlorohydrin (549). p-Methoxy-β-chlorostyrene was obtained by heating the ethyl ether of the corresponding chlorohydrin (583).

When styrylmagnesium bromide was treated with benzenesulfonyl chloride, a 40 per cent yield of β-chlorostyrene was obtained along with 34 per cent of 1,4-diphenylbutadiene and 33.6 per cent of styrene (from the unreacted Grignard reagent) (260). β-Chlorostyrene was also a by-product of the reaction between phenylmagnesium bromide and 1,1,2,2-tetrachloroethane or 1,1-dichloro-2,2-difluoroethane (723).

p-Methyl-β-chlorostyrene was the only product isolated from the treatment of p-methylstyrene with nitrosyl chloride (555). β-Chlorostyrene and styrene were the products obtained by treating α-hydroxy-β,β,β-trichloroethylbenzene with zinc in alcohol (799).

When heated with concentrated alcoholic potassium hydroxide at 180°C. in a sealed tube β-chlorostyrene yielded β-ethoxystyrene (207, 227). This same result has been effected with alcoholic sodium ethoxide (207) with a yield of 67 per cent (197).

$$C_6H_5CH{=}CHCl + C_2H_5ONa \xrightarrow[180°C.]{C_2H_5OH} C_6H_5CH{=}CHOC_2H_5 + NaCl$$

(67 per cent)
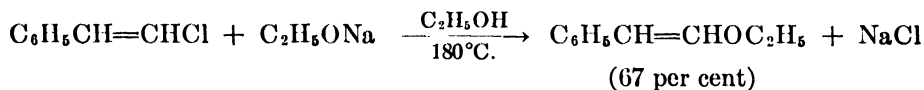
In the case of o-hydroxy-β-chlorostyrene boiling with alcoholic potassium hydroxide produced benzofuran (404, 405).
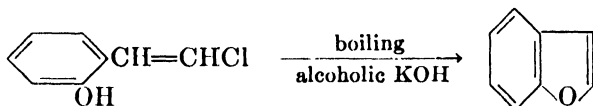
When o-amino-β-chlorostyrene was heated with sodium ethoxide at 160–170°C., indole was obtained (453). With o-methylamino-β-chlorostyrene, N-methyl-indole and o-aminophenylacetylene were produced (454).
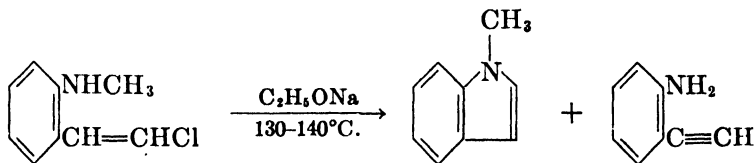
However, toward most hydrolytic agents β-chlorostyrene is comparatively inert. Toward potassium hydroxide the order of ease of hydrolysis is as follows: $C_6H_5CCl{=}CHCl > C_6H_5CCl{=}CH_2 > C_6H_5CH{=}CCl_2 > C_6H_5CH{=}CHCl$; toward piperidine: $C_6H_5CCl{=}CHCl > C_6H_5CH{=}CHCl > C_6H_5CCl{=}CH_2 > C_6H_5CH{=}CCl_2$; and toward silver nitrate: $C_6H_5CCl{=}CH_2 > C_6H_5CCl{=}CHCl > C_6H_5CH{=}CHCl > C_6H_5CH{=}CCl_2$ (559). At 41°C. the order of ease of hydrolysis with alcoholic potassium hydroxide of the nitro-β-chlorostyrenes

was: p-nitro > o-nitro > m-nitro> unsubstituted (150°. At 81°C. the last two were reversed. Which halogen atoms were removed was not determined.

Phenyllithium in ether solution dehydrohalogenated β-chlorostyrene to give a 70 per cent yield of phenylacetylene (782). With butyllithium the yield of phenylacetylene was 82 per cent (781). The following mechanism was advanced, since the ether solution, when treated with benzophenone before hydrolysis, yielded 93 per cent of triphenylpropargyl alcohol:

$$C_6H_5CH{=}CHCl + C_4H_9Li \rightarrow [C_6H_5CLi{=}CClLi] - \rightarrow$$

$$\begin{array}{c} & & C_6H_5C{\equiv}CH \\ & \nearrow & \\ H_2O & & \\ [C_6H_5C{\equiv}CHLi] & & \\ (C_6H_5)_2CO & \searrow & \\ & & C_6H_5C{\equiv}CCOH(C_6H_5)_2 \end{array}$$
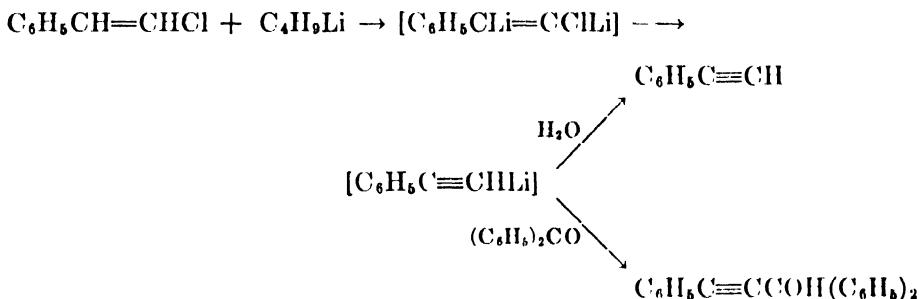
When heated with butyllithium in benzene at 50°C. for 22 hr., β-chlorostyrene yielded 20 per cent of phenylacetylene and 53 per cent of β-butylstyrene.

When β-chlorostyrene was heated with hydrochloric acid at 170–180°C., the product was β-phenylnaphthalene (40). With p-methyl-β-chlorostyrene or p-methyl-β,β-dichloroethylbenzene and water at 170–180°C., the product was 2-(p-methylphenyl) methylnaphthalene.

Pyrolysis of β-chloro styrene in a porcelain tube at 550–600°C. yielded hydrogen chloride and acetylene (209). Phenylacetylene was postulated as one of the intermediates.

With nitrosyl chloride β-chlorostyrene yielded difficultly separable mixtures (555).

C. α-Chlorostyrene chemistry

α-Chlorostyrene probably was first prepared by Laurent (435) in 1844 by treating styrene dichloride with potassium hydroxide. Shortly thereafter Blyth and Hofmann (87) observed the same reaction. The correct structure for α-chlorostyrene was first postulated by Friedel (237, 239, 240) in 1868, who prepared it by treating acetophenone with phosphorus pentachloride. Generally the product isolated was a mixture of α-chlorostyrene and α,α-dichloroethylbenzene. Treatment of the latter with alcoholic potassium hydroxide yielded α-chlorostyrene. In 1870 Glaser (269) prepared α-chlorostyrene by distilling styrene dichloride from lime. He formulated the compound as the β-isomer. Erlenmeyer (204) later showed this to be wrong, since the properties were the same as those of Friedel's α-chlorostyrene.

The preparation of α-chlorostyrene from styrene dichloride has been mentioned above and discussed in detail under the reactions of the latter compound

The commonest route to α-chlorostyrenes has been from the corresponding aceto-phenones with or without the isolation of the intermediate α,α-dichloroethyl-

$$ArCOCH_3 \xrightarrow{PCl_5} ArCCl_2CH_3 \xrightarrow[KOH + C_2H_5OH]{heat\ or} ArCCl{=}CH_2$$
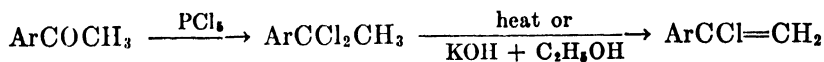
benzene. If the reaction is conducted below 40°C., the dichloroethylbenzene is the only product of the reaction (430, 431). By-products have included dypnone (732) and ω,ω-dichloro-ω-tetrachlorophosphinoacetophenone. A number of in-vestigators (34, 103, 104, 449, 632) have prepared α-chlorostyrene by this method

TABLE 9

α-Chlorostyrenes from substituted acetophenones

SUBSTITUTED ACETOPHENONE	YIELD OF α-CHLOROSTYRENE	REFERENCE
	per cent	
p-Methyl ..		(39, 354)
2,4-Dimethyl...	82	(762)
	86	(276)
2,4,6-Trimethyl* .	50	(4)
	78	(762)
2,3,4,6-Tetramethyl* ..	73	(4)
p-Chloro		(803)
	60	(762)
p-Bromo...		(173, 803)
2,4,6-Trimethyl-3-bromo*...	63	(5)
o-Nitro..		(259)
p-Nitro.		(166)

* In the case of 2,4,6-trimethyl, 2,3,4,6-tetramethyl, and 2,4,6-trimethyl-3-bromo, 19, 22, and 11.5 per cent, respectively, of the corresponding phenacyl chlorides were isolated as by-products (4, 5).

and have given yields of 54 per cent (174) to 91 per cent (531). The substituted α-chlorostyrenes listed in table 9 also have been prepared in this way.

α-Chlorostyrene has been prepared in 70 per cent yield by treating α-chloro-β-bromoethylbenzene with alcoholic potassium hydroxide at 0°C. (759). It is also a by-product of the coupling of phenylacetylene (802).

$$C_6H_5C{\equiv}CH \xrightarrow[HCl]{CuCl,\ NH_4Cl} C_6H_5C{\equiv}C{-}C{\equiv}CC_6H_5 + C_6H_5CCl{=}CH_2$$
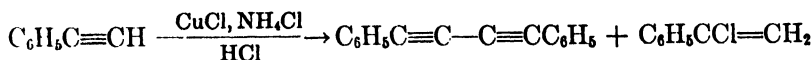
α-Chlorostyrene and its homologs have been used primarily as intermediates for the preparation of phenylacetylenes. This reaction was observed first by

Friedel (237, 239, 240), who obtained phenylacetylene by treating α-chlorostyrene or a mixture of α-chlorostyrene and α,α-dichloroethylbenzene with alcoholic potassium hydroxide at 120°C. While such mixtures have been used, most investigators have preferred to isolate the α-chlorostyrene before proceeding with further dehydrohalogenation. The yields of phenylacetylene from α,α-dichloroethylbenzene are low using aqueous potassium hydroxide (516), soda lime (516), or red-hot sodium hydroxide (522), even though α,α-dichloroethylbenzene is more reactive toward potassium hydroxide than is β,β-dichloroethylbenzene (558).

With α-chlorostyrene 38 per cent of the halogen was removed in 1 hr. by 24

TABLE 10

Phenylacetylenes from α-chlorostyrenes

SUBSTITUTED α-CHLOROSTYRENE	REAGENT	YIELD	REFERENCE
		per cent	
p-Methyl	NaNH$_2$ in liquid NH$_3$	49	(763)
	Na in liquid NH$_3$	63	(761)
	Alcoholic KOH	25	(354)
2,4-Dimethyl	NaNH$_2$	70–72	(276)
	NaNH$_2$ at 150°C.	75	(762)
2,4,6-Trimethyl	NaNH$_2$ at 150°C.	71	(762)
2,3,4,6-Tetramethyl	C$_2$H$_5$ONa + C$_2$H$_5$OH, 110°C.	65	(4)
p-Chloro.	25% alcoholic KOH	36	(762)
p-Chloro*	25% alcoholic KOH		(803)
p-Bromo*	25% alcoholic KOH		(803)
p-Bromo†	25% alcoholic KOH	53	(173)
2,4,6-Trimethyl-3-bromo	C$_2$H$_5$ONa + C$_2$H$_5$OH	57	(5)

* From the monohalide and dihalide mixture.
† From the dichloride only.

per cent alcoholic potassium hydroxide at 80°C. and 78 per cent in 3 hr. by the same reagent at 120°C. (174). Other investigators have used alcoholic sodium

$$C_6H_5CCl{=}CH_2 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}} C_6H_5C{\equiv}CH$$

ethoxide at 110–130°C. (37–43 per cent yield) (531) and sodium amide in liquid ammonia (57 per cent yield) (763). In the former case a small amount of β-ethoxystyrene appeared as a by-product (531). With sodium in liquid ammonia the only product isolated was 15 per cent of ethylbenzene (761).

Substituted α-chlorostyrenes have been converted to the corresponding phenylacetylenes by means of a variety of reagents (see table 10).

In the presence of hot water (206) or hot aqueous acids, α-chlorostyrene is hydrolyzed to acetophenone. With concentrated hydrochloric acid alone (60), yields of 30 per cent (193) to 77 per cent (759) have been reported. With hydrochloric acid and metal halides the yields were 74–78 per cent (193) and with 80
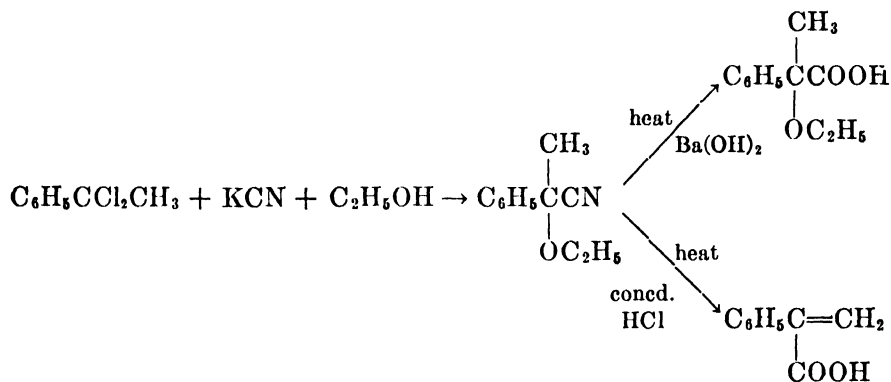
$$C_6H_5CCl{=}CH_2 \xrightarrow[\text{HCl}]{\text{concd.}} C_6H_5COCH_3$$

$$\text{(30–77 per cent)}$$
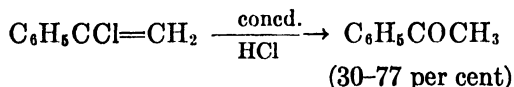
per cent sulfuric acid at 60°C. 81 per cent (192, 197). With saturated aqueous hydrochloric acid the reaction also has been reported to proceed with explosive violence to give appreciable quantities of 1,3,5-triphenylbenzene. This compound also has been prepared by treating α-chlorostyrene with boron fluoride (479) and by heating α,α-dichloroethylbenzene with water (60).

When treated with nitrosyl chloride α-chlorostyrene yielded α,β,β-trichlorostyrene and α,β-dichloro-β-nitrostyrene (555). α-Chlorostyrene reacted with

$$C_6H_5CCl{=}CH_2 \xrightarrow{\text{NOCl}} C_6H_5CCl{=}CCl_2 + C_6H_5CCl{=}CClNO_2$$
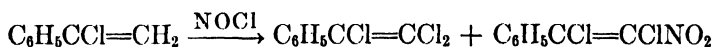
alcoholic potassium cyanide at 200–220°C. to give in low yield a compound which could be hydrolyzed with barium hydroxide to phenylsuccinic acid (632).

Besides the α,α-dichloroethylbenzene chemistry discussed in connection with α-chlorostyrene it should be mentioned that α,α-dichloroethylbenzene also has been obtained by chlorinating ethylbenzene in the sunlight (588). Treatment with aqueous silver oxide yielded acetophenone. In the cold α,α-dichloroethylbenzene reacted with alcoholic potassium cyanide to give α-methyl-α-ethoxyphenylacetonitrile, some of whose chemistry follows (430, 431).

$$C_6H_5CCl_2CH_3 + KCN + C_2H_5OH \rightarrow C_6H_5\underset{\underset{OC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}CN$$

with branches:

heat / Ba(OH)₂ → $C_6H_5\underset{OC_2H_5}{\overset{CH_3}{C}}COOH$

concd. HCl / heat → $C_6H_5C{=}CH_2$ with COOH

D. More highly chlorinated styrene derivatives

As has been mentioned previously, β,β-dichloroethylbenzene can be obtained by treating phenylacetaldehyde with phosphorus pentachloride (40, 227). A

number of substituted β,β-dichloroethylbenzenes have been prepared by heating 1-methyl-1-dichloromethyl-4-methylenedihydrobenzenes.
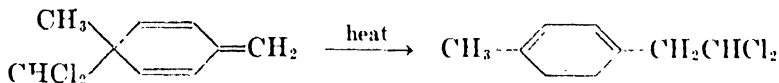
The analogs prepared in this way include p-methyl- (37), 2,4-dimethyl- (41), 3,4-dimethyl- (41), 2,4,5-trimethyl- (41), 2-chloro-4-methyl- (32), 2,6-dichloro-4-methyl- (32), and 2,4-dimethyl-6-chloro- (32). α,p-Dimethoxy-β,β-dichloroethylbenzene has been obtained by treating α,p-dimethoxy-β,β,β-trichloroethylbenzene with zinc and acetic acid (501).

The conversion of these compounds to β-chlorostyrenes has been mentioned previously. Otherwise they are quite inert. Treatment of p-methyl-β,β-dichloroethylbenzene with chromic acid in acetic acid yielded p-(β,β-dichloroethyl)-benzoic acid (40). This was reduced to p-ethylbenzoic acid with sodium and alcohol.
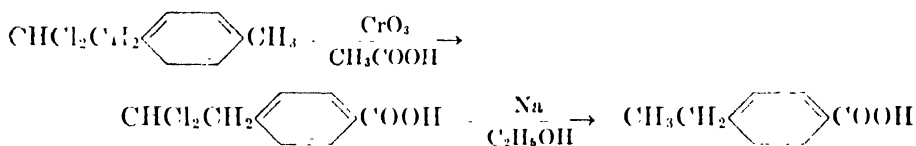
Meldrum and coworkers have described a large number of compounds as derivatives of β,β-dichloroethylbenzene which they obtained by treating β,β,β-trichloro-α-hydroxyethylbenzenes with zinc and acetic acid. In 1910 Dharwarkar and Alimchandani (160) showed that all of these compounds are actually β,β-dichlorostyrenes. This is not surprising, since as early as 1897 Biltz (81) showed that β,β-dichlorostyrene was one of the products obtained by treating benzene with chloral in the presence of aluminum chloride. Very shortly thereafter the acetates of β,β,β-trichloro-α-hydroxyethylbenzene (800) and o-methoxy-β,β,β-trichloro-α-hydroxyethylbenzene (437) were treated with zinc to give 90 per cent and 80 per cent, respectively, of the corresponding β,β-dichlorostyrenes. In the latter case a little of the acetate of the corresponding β,β-dichloro-α-hydroxyethylbenzene also was isolated.

(80 per cent)
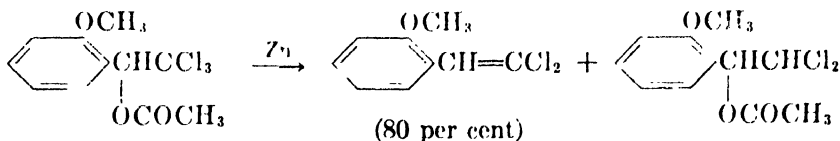
In 1905 Dinesmann (163) obtained β,β-dichlorostyrene by treating β,β,β-trichloro-α-hydroxyethylbenzene with zinc and acetic acid. 3-Carboxy-4-hydroxy-β,β-dichlorostyrene has been prepared similarly (133).

Dharwarkar and Alimchandani used the following reactions to prove the structures of their β,β-dichlorostyrenes:
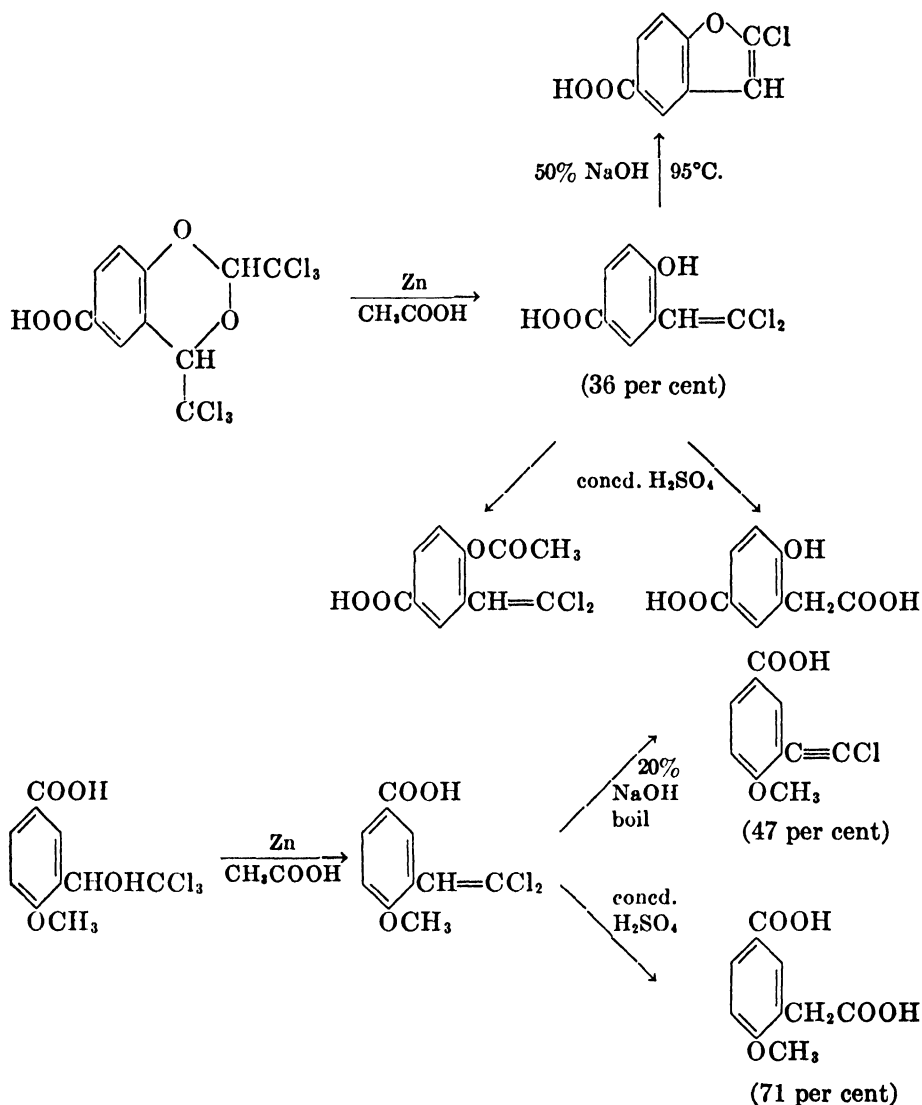
Besides the 2-hydroxy-5-carboxy- and 2-methoxy-5-carboxy-β,β-dichlorostyrenes shown above, the 3-carboxy-4-hydroxy- (86 per cent yield), 3-carboxy-4-methoxy-, 2-carboxy-4-hydroxy-, and 2-carboxy-4-methoxy- analogs also were prepared. Both the 2-hydroxy-5-carboxy- and the 3-carboxy-4-hydroxy-β,β-dichlorostyrenes were converted to the corresponding phenylacetic acids by means of concentrated sulfuric acid. These two styrenes also were acetylated and were converted to the methoxy compounds with methyl sulfate. 3-Carboxy-4-methoxy-β-chlorophenylacetylene was prepared from the corresponding β,β-dichloro-styrene by treatment with hot aqueous sodium hydroxide.

β,β-Dichlorostyrenes formulated as β,β-dichloroethylbenzenes, which were prepared by Meldrum and coworkers, are listed in table 11. These β,β-dichlorostyrenes were prepared by treating the indicated starting compound with zinc and acetic acid.

A number of β,β-dichlorostyrenes, formulated as β,β-dichloroethylbenzenes, were converted to the corresponding phenylacetic acids, as shown in table 12.

Other than the reactions described above with concentrated sulfuric acid and with hot alkali, Meldrum and coworkers found these compounds to be surprisingly inert. Thus 2-carboxy-4,5,5-triacetoxy-β,β-dichlorostyrene was easily deacetylated by means of sulfuric acid in methanol (502). 2-Carboxy-4-methyl-6-hydroxy-β,β-dichlorostyrene was acetylated with acetic anhydride containing sulfuric acid (503). 3-Carboxy-4-methoxy-β,β-dichlorostyrene yielded a methyl ester, amide, anilide, and p-toluidide (321). It was demethylated with hydriodic
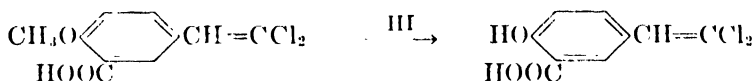
acid. Treatment with aqueous sodium hydroxide at 165°C. was reported to yield 3-carboxy-4-methoxyphenylacetaldehyde.

Besides the route from β,β,β-trichloro-α-hydroxyethylbenzene, β,β-dichlorostyrene has been prepared by treating α,β,β-trichloroethylbenzene (from β-chlorostyrene and chlorine) with alcoholic potassium hydroxide (85). p-Methyl-β,β-dichlorostyrene has been prepared similarly from p-methyl-β,β,β-trichloroethylbenzene (38, 81).
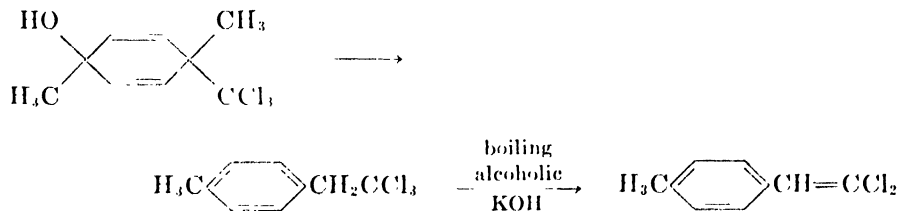
α,2-Diacetoxy-ω-carboxy-β,β-dichlorostyrene was obtained by treating 2-hydroxy-5-carboxy-β,β-dichloroacetophenone with acetic anhydride and sodium acetate (138).
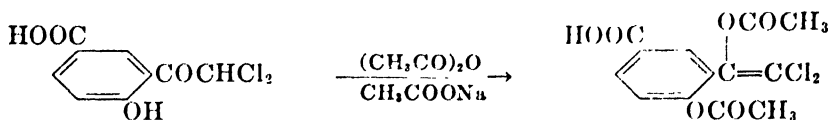
β,β-Dichlorostyrene adds chlorine or bromine (85). With alcoholic potassium hydroxide at 100°C. the chief product (41 per cent yield) was β-chlorophenylacetylene along with some β-chloro-β-ethoxystyrene (531). The latter compound
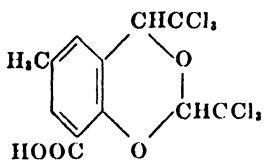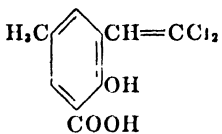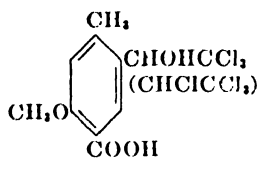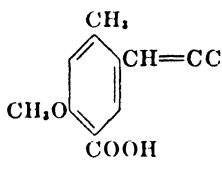
TABLE 11

Preparations of β,β-dichlorostyrenes

STARTING COMPOUND	β,β-DICHLOROSTYRENE OBTAINED	YIELD	REFERENCE
		er cent	
H_3C—ring—$CHCCl_3$ / $CHCCl_3$ with O, O, HOOC	H_3C—ring—$CH=CCl_2$, OH, COOH		(14)
CH_3—ring—$CHOHCCl_3$ $(CHClCCl_3)$, CH_3O, COOH	CH_3—ring—$CH=CCl_2$, CH_3O, COOH		(498, 499)
$O=C-O$—ring—$CHCCl_3$, OH, CH_3	COOH—ring—$CH=CCl_2$, OH, CH_3		(500)
$O=C-O$—ring—$CHCCl_3$, CH_3O, CH_3	COOH—ring—$CH=CCl_2$, CH_3O, CH_3		(500)
H_3C—ring—$CHCCl_3$ $>O$ / $C=O$, HO, CH_2COOH	H_3C—ring—$CH=CCl_2$, HO—COOH, CH_2COOH		(500)
CH_3COO—ring—$CHCCl_3$, $OCOCH_3$	CH_3COO—ring—$CH=CCl_2$		(501)
C_6H_5COO—ring—$CHCCl_3$, $OCOC_6H_5$	C_6H_5COO—ring—$CH=CCl_2$		(501)
CH_3COO—ring—$CHCCl_3$, $OCOCH_3$, $OCOCH_3$	CH_3COO—ring—$CH=CCl_2$, $OCOCH_3$		(501)

TABLE 11—*Continued*

STARTING COMPOUND	β,β-DICHLOROSTYRENE OBTAINED	YIELD	REFERENCE
		per cent	

Starting compound	β,β-dichlorostyrene obtained	Yield	Reference
OCOCH₃ ring with CH₃COO, CCl₃CH, OCOCH₃, CHCCl₃, OCOCH₃	OCOCH₃ ring with CH₃COO, CCl₂=CH, CH=CCl₂		(501)
OCOC₆H₅ ring with C₆H₅COO, CCl₃CH, OCOC₆H₅, CHCCl₃, OCOC₆H₅	OCOC₆H₅ ring with C₆H₅COO, CCl₂=CH, CH=CCl₂		(501)
CH₃COO, CH₃COO, CH₃COO ring with CHCCl₃, >O, CO	CH₃COO, CH₃COO, CH₃COO ring with CH=CCl₂, COOH		(502)
OH, HO, HO ring with CHCCl₃, >O, CO, CH₂COOH	OH, HO, HO ring with CH=CCl₂, COOH, CH₂COOH		(502)
CH₃O, CH₃O, CH₃O ring with CHCCl₃, >O, CO	CH₃O, CH₃O, CH₃O ring with CH=CCl₂, COOH		(502)
CH₃O, CH₃O, CH₃O ring with CClCCl, >O, CO, CH₂COOH	CH₃O, CH₃O, CH₃O ring with CH=CCl₂, COOH, CH₂COOH		(502)
CH₃O, CH₃O ring with CHCCl₂, >O, CO	CH₂O, CH₃O ring with CH=CCl₂, COOH		(502)
HO, H₃C ring with CHCCl₃, >O, CO	HO, H₃C ring with CH=CCl₂, COOH	75	(503)

TABLE 11—*Continued*

STARTING COMPOUND	β,β-DICHLOROSTYRENE OBTAINED	YIELD per cent	REFERENCE
CH_3, $CHCCl_3$, $>O$, HO, CO (benzene ring)	CH_3, $CH=CCl_2$, HO, $COOH$ (benzene ring)		(503)
CH_3O, $CHCCl_3$, $>O$, H_2C, CO (benzene ring)	CH_3O, $CH=CCl_2$, H_2C, $COOH$ (benzene ring)	75	(503)
CH_3, $CHCCl_3$, $>O$, CH_3O, CO (benzene ring)	CH_3, $CH=CCl_2$, CH_3O, $COOH$ (benzene ring)	70	(503)
CH_3, $CHOHCCl_3$, CH_3O, $COOH$, CH_2COOH (benzene ring)	CH_3, $CH=CCl_2$, CH_3O, $COOH$, CH_2COOH (benzene ring)	67	(503)
CH_3O, $CHCCl_3$, $>O$, H_3C, CO, CH_2COOH (benzene ring)	CH_3O, $CH=CCl_2$, H_3C, $COOH$, CH_2COOH (benzene ring)	33	(503)
CH_3O — ring — $CHOHCCl_3$, $HOOC$	CH_3O — ring — $CH=CCl_2$, $HOOC$	69	(321)
HO — ring — $CHCCl_3$, $C-O$, O	HO — ring — $CH=CCl_2$, $COOH$		(321)
CH_3O — ring — $CHCCl_3$, $C-O$, O	CH_3O — ring — $CH=CCl_2$, $COOH$		(321)
$HOOC$ — ring — $CHOHCCl_3$, OCH_3	$HOOC$ — ring — $CH=CCl_2$, OCH_3		(321)

TABLE 12
Phenylacetic acids from β,β-dichlorostyrenes

β,β-DICHLOROSTYRENE	PHENYLACETIC ACID OBTAINED	REAGENT	YIELD	REFERENCE
			per cent	
HOOC⟨⟩CH=CCl₂ / CH₃O ... CH₃	HOOC⟨⟩CH₂COOH / CH₃O ... CH₃	Concentrated H₂SO₄		(499)
⟨⟩COOH / H₃C ... CH=CCl₂ / OH	⟨⟩COOH / H₃C ... CH₂COOH / OH	Concentrated H₂SO₄		(500)
H₃C⟨⟩CH=CCl₂ / CH₃O ... COOH	H₃C⟨⟩CH₂COOH / CH₃O ... COOH	Concentrated H₂SO₄		(500)
H₃C⟨⟩CH=CCl₂ / HO ... COOH / CH₂COOH	H₃C⟨⟩CH₂COOH / HO ... COOH / CH₂COOH	Concentrated H₂SO₄		(500)
CH₃COO / CH₃COO⟨⟩CH=CCl₂ / CH₃COO ... COOH	OH / HO⟨⟩CH₂COOH / HO ... COOH	Concentrated H₂SO₄		(502)
CH₃COO / CH₃COO⟨⟩CH=CCl₂ / CH₃COO ... COOH / CH₂COOH	OH / HO⟨⟩CH₂COOH / HO ... COOH / CH₂COOH	Concentrated H₂SO₄		(502)
CH₃O / CH₃O⟨⟩CH=CCl₂ / CH₃O ... COOH	CH₃O / CH₃O⟨⟩CH₂COOH / CH₃O ... COOH	Concentrated H₂SO₄		(502)
CH₃O / CH₃O⟨⟩CH=CCl₂ / CH₃O ... COOH / CH₂COOH	CH₃O / CH₃O⟨⟩CH₂COOH / CH₃O ... COOH / CH₂COOH	Concentrated H₂SO₄		(502)

TABLE 12—*Continued*

β,β-DICHLOROSTYRENE	PHENYLACETIC ACID OBTAINED	REAGENT	YIELD	REFER-ENCE
			per cent	
CH₃COO ... CH=CCl₂ / CH₃COO ... COOH	OH ... CH₂COOH / HO ... COOH	Concentrated H₂SO₄		(502)
OH ... CH=CCl₂ / H₃C ... COOH	OH ... CH₂COOH / H₃C ... COOH	Concentrated H₂SO₄		(503)
CH₃O ... CH=CCl₂ / H₃C ... COOH	CH₃O ... CH₂COOH / H₃C ... COOH	Concentrated H₂SO₄	82	(503)
CH₃ ... CH=CCl₂ / CH₃O ... COOH	CH₃ ... CH₂COOH / CH₃O ... COOH	Concentrated H₂SO₄	82	(503)
CH₃ ... CH=CCl₂ / CH₃O ... COOH ... CH₂COOH	CH₃ ... CH₂COOH / CH₃O ... COOH ... CH₂COOH	Concentrated H₂SO₄	68	(503)
H₃C ... CH=CCl₂ / OH ... COOH	H₃C ... CH₂COOH / OH ... COOH	KOH, 250–260°C.		(14)
CH=CCl₂ / OCH₃	CH₂COOH / OCH₃	KOH, C₂H₅OH		(437)

was obtained from the acetylene by treatment with alcoholic sodium ethoxide or potassium hydroxide.

$$C_6H_5CH{=}CCl_2 \xrightarrow[\text{C}_2\text{H}_6\text{OH}]{\text{KOH}} C_6H_5C{\equiv}CCl \quad + \quad C_6H_5CH{=}CClOC_2H_5$$

KOH or C₂H₅ONa

C₂H₅OH
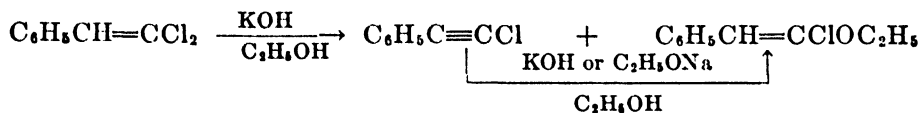
In 1877 Dyckerhoff found that treatment of phenacyl chloride with phosphorus pentachloride yielded α,α,β-trichloroethylbenzene, which decomposed on distillation to give α,β-dichlorostyrene (179, 180). The compound added chlorine

$$C_6H_5COCH_2Cl + PCl_5 \rightarrow POCl_3 + C_6H_5CCl_2CH_2Cl \xrightarrow{\text{distillation}} C_6H_5CCl=CHCl$$
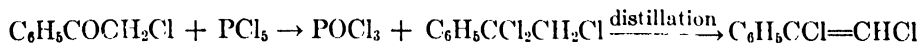
and bromine, but did not react with alcoholic potassium cyanide (180). The study of these compounds was extended in considerable detail by Kunckell and co-workers.

Most α,β-dichlorostyrenes have been prepared by treating the corresponding phenacyl chloride with phosphorus pentachloride, as shown above. The compounds thus prepared are listed in table 13.

The following divinyl compounds also were prepared (423): 4-methoxy-1,2-di(α,β-dichlorovinyl)benzene, 2,4,6-trimethyl-1,3-di(α,β-dichlorovinyl)benzene, 2,4,6-triethyl-1,3-di(α,β-dichlorovinyl)benzene, and 4,4'-di(α,β-dichlorovinyl)phenyl ether. When p-methoxyphenacyl chloride was heated with phosphorus pentachloride over a free flame, some ring chlorination also occurred.
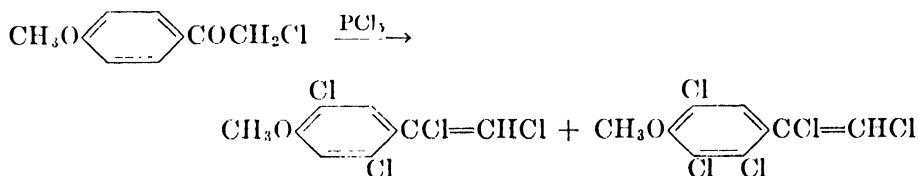
The same reaction was observed with 3,4-di(chloroacetyl)anisole.
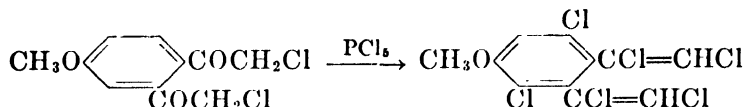
α,β-Dichlorostyrene has been prepared by treating α,β-diiodostyrene with mercurous chloride (550). 2-Methoxy-5-carboxy-α,β-dichlorostyrene and 2-methoxy-5-nitro-α,β-dichlorostyrene have been obtained from the corresponding α,β,β-trichloroethylbenzenes (prepared by treating anisic acid and p-nitroanisole, respectively, with dichloroacetaldehyde in the presence of sulfuric and hydrochloric acids) by treatment with alcoholic potassium hydroxide (137).
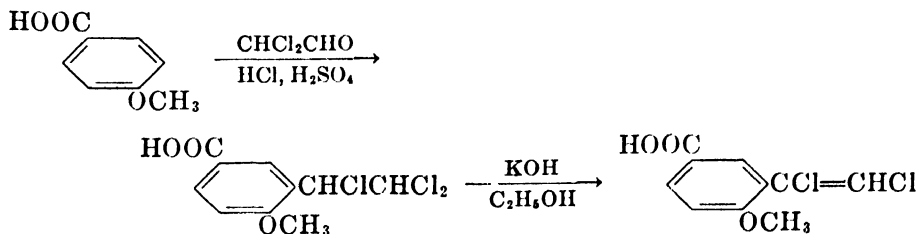
3-Carboxy-4-methoxy-α,β-dichlorostyrene was produced by treating 3-carboxy-4-methoxy-β-chlorophenylacetylene with hydrogen chloride in chloroform solution (160).
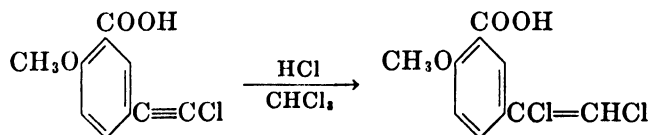
When α,β-dichlorostyrenes are treated with alcoholic potassium hydroxide, β-chlorophenylacetylenes are produced.

$$\text{ArCCl}{=}\text{CHCl} \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}} \text{ArC}{\equiv}\text{CCl}$$
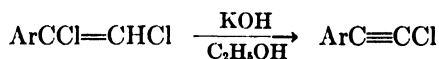
The following substituted β-chlorophenylacetylenes have been prepared in this way: p-methyl- (423, 424), 2,5-dimethyl- (423, 424), p-ethyl- (425), p-isopropyl-

TABLE 13

α,β-Dichlorostyrenes from phenacyl chlorides

α,β-DICHLOROSTYRENE	REFERENCES
p-Methyl....................	(424, 803)
p-Methyl (65 per cent yield)..........	(423)
2,4-Dimethyl.....	(423, 424)
2,5-Dimethyl...........	(423, 424)
3-Chloro-4-methyl........	(424)
p-Ethyl..	(423, 425)
p-Isopropyl.....	(423, 425)
2,4,6-Trimethyl....	(425)
2-Methyl-5-isopropyl.	(423, 425)
p-Methoxy..	(421, 423)
2-Bromo-5-methoxy	(423)
p-Ethoxy...	(423)
2-Methyl-5-methoxy	(423)
2,4-Dimethoxy	(423)
2,4,6-Triethyl.	(423)

(425), 2,4,6-trimethyl- (425), 2-methyl-5-isopropyl- (425), p-methoxy- (422) in 10 per cent yield (423), 2-methyl-5-methoxy- (423), and 2,4-6-triethyl- (423). When α,β-dichlorostyrenes are treated with sodium in ether, phenylacetylenes are produced. This method has been used for the preparation of the following

$$\text{ArCCl}{=}\text{CHCl} \xrightarrow[\text{ether}]{\text{Na}} \text{ArC}{\equiv}\text{CH}$$
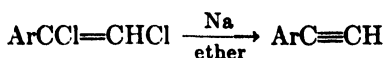
phenylacetylenes: p-methyl- (423, 424, 803), p-ethyl- (423, 425), p-isopropyl- (423, 425), 2,4,6-trimethyl- (425), 2-methyl-5-isopropyl- (423, 425), p-methoxy- (422, 423), 2-methyl-5-methoxy- (423), and 2,4,6-triethyl- (423).

With phenylhydrazine or N-methyl-N-phenylhydrazine p-methyl-α,β-dichlorostyrene yielded the corresponding bisphenylhydrazone of phenylglyoxal (426).

$$H_3C\langle\rangle CCl{=}CHCl + 3C_6H_5NHNH_2 \longrightarrow$$

$$H_3C\langle\rangle\underset{\underset{NHNC_6H_5}{\|}}{C}CH{=}NNHC_6H_5$$
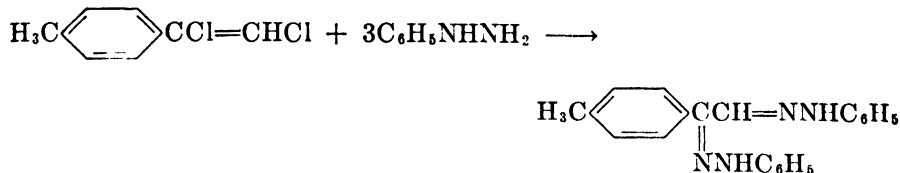
With ammonia both α,β-dichlorostyrene and p-methyl-α,β-dichlorostyrene gave a symmetrically substituted pyridazine (427).

$$C_6H_5CCl{=}CHCl + NH_3 \xrightarrow[\text{12--18 hr.}]{\text{180--200°C.}}$$
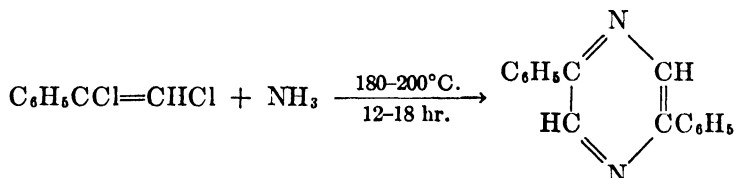
2-Methoxy-5-nitro-α,β-dichlorostyrene added chlorine to give 2-methoxy-5-nitro-$\alpha,\alpha,\beta,\beta$-tetrachloroethylbenzene (137). Treatment of this latter compound with alcoholic potassium hydroxide yielded 2-methoxy-5-nitro-α,β,β-trichlorostyrene. α,β,β-Trichlorostyrene itself has been prepared from β,β-dichlorostyrene by a similar series of reactions (85). The same method has been used for

$$C_6H_5CH{=}CCl_2 \xrightarrow[\text{CHCl}_3]{Cl_2} C_6H_5CHClCCl_3 \xrightarrow[\text{C}_2H_5OH]{KOH} C_6H_5CCl{=}CCl_2$$
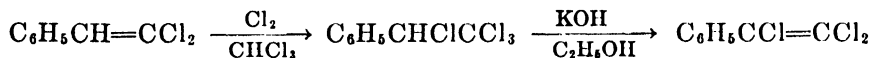
the preparation of 2-methyl-4-methoxy-5-carboxy-α,β,β-trichlorostyrene (499) and 2-methoxy-5-nitro-α,β,β-trichlorostyrene (136). In these two latter cases the α,β,β,β-tetrachloroethylbenzenes were obtained from the α-hydroxy-β,β,β-trichloroethylbenzenes by treatment with hydrogen chloride and sulfuric acid.

α,β,β-Trichlorostyrene also was one of the products of the reaction between benzoyl peroxide and tetrachloroethylene (616). It was the principal product

$$(C_6H_5COO)_2 + C_2Cl_4 \xrightarrow{\text{110--115°C.}} C_6H_5Cl + 2CO_2 + C_6H_5CCl{=}CCl_2$$

(27 per cent yield) when pentachloroethylbenzene and hydrogen fluoride were heated in an iron vessel (772, 773). Some fluorodichlorostyrene (14 per cent) also was obtained. In a nickel vessel the trichlorostyrene was the by-product and the principal product was 65 per cent of difluorotrichloroethylbenzene (772).

α,β,β-Trichlorostyrene adds both chlorine and bromine, although the reactions are quite slow (85). The preparation of many of the side-chain chlorinated derivatives of p-chlorostyrene has been described recently (786a).

IV. BROMINATED DERIVATIVES

A. Addition of bromine

Probably the most widely used reaction for the characterization of styrene and substituted styrenes is the addition of bromine. The reaction proceeds easily and the dibromides thus obtained are crystalline solids with characteristic melting points.

$$RCH{=}CH_2 + Br_2 \rightarrow RCHBrCH_2Br$$
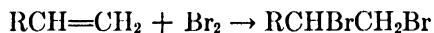
Styrene dibromide was first prepared by Kopp in 1844 (411). In 1845 Blyth and Hofmann (87) also added bromine to styrene. This reaction was reported by all of the earlier investigators: Erlenmeyer (1866) (203), Swarts (1866) (722), Berthelot (1866–68) (72, 75, 76, 77, 78, 80), Friedel (1868) (238), and Glaser (1870) (269). The alternative preparation by the bromination of ethylbenzene was first mentioned by Thorpe in 1871 (739) and by Radziszewski in 1873 (589).

Since these early reports the addition of bromine to styrene has been described in numerous articles. (These include the following references: 31, 63, 105, 117, 175, 177, 181, 214, 215, 222, 253, 256, 283, 320, 392, 513, 543, 569, 629, 640, 645, 691, 710, 797, 811.) Many inert solvents have been used, but the best conditions seem to be an ether solvent at 0°C. (98 per cent yield) (214) or −10°C. (quantitative yield) (177), a chloroform solvent in the cold (theoretical bromine absorption) (253), or a liquid sulfur dioxide solvent (theoretical yield) (628a, 629). If properly conducted, the addition evidently is quantitative.

The addition of bromine to styrene is practically instantaneous (535) and the heat of the reaction has been measured (459). The kinetics have been studied, although in glacial acetic acid solution the addition is too fast for detailed measurements (749). The reaction has been included in several studies of competitive bromine addition (22, 345). In the presence of oxygen some of the latter element also is absorbed (89). The products were styrene dibromide and an unidentified oil.

In methanol solution side reactions occur and the addition is not complete. Bromine absorption has been shown to be 85 per cent of theory (254). Under the same conditions (bromine and sodium bromide in methanol) another investigator found the products to be 50 per cent styrene dibromide and 50 per cent bromostyrene, together with some hydrogen bromide (356). Some addition of the methoxyl radical also has been observed (490).

Unlike the chlorination, the bromination of ethylbenzene in the dark at its boiling point gives primarily styrene dibromide (661). In the light α,α-dibromoethylbenzene is obtained. The first bromine enters the α-position. This bromina-

$$C_6H_5CH_2CH_3 \xrightarrow{\text{Br}_2} C_6H_5CHBrCH_3 \xrightarrow{\text{Br}_2} C_6H_5CHBrCH_2Br$$

tion of ethylbenzene or of α-bromoethylbenzene has been utilized by several investigators for the preparation of styrene dibromide (26, 105, 242, 308, 811; in 90 per cent yield, 115).

Styrene dibromide constituted 20 per cent of the product obtained by treating styrene with bromine chloride (759).

$$C_6H_5CH{=}CH_2 + BrCl \xrightarrow{-10°C.}$$

$$C_6H_5CHClCH_2Cl + C_6H_5CHClCH_2Br + C_6H_5CHBrCH_2Br$$
$$\text{(65–70 per cent)} \qquad \text{(20 per cent)}$$
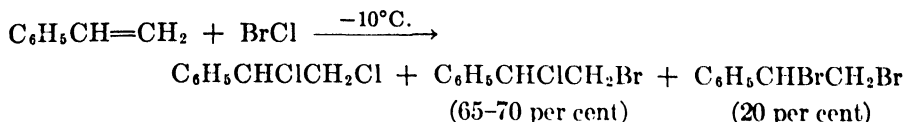
It has been obtained by treating styrene with N-bromoacetamide in acetone solution (783) and has been reported as a by-product of the reaction between phenylacetylene and hydrobromic acid in acetic acid solution (733).

$$C_6H_5C{\equiv}CH \xrightarrow[\text{CH}_3\text{COOH}]{\text{HBr}} \begin{matrix} C_6H_5 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} C{=}CHCOC_6H_5 +$$

$$C_6H_5COCH_3 + C_6H_5CHBrCH_2Br$$
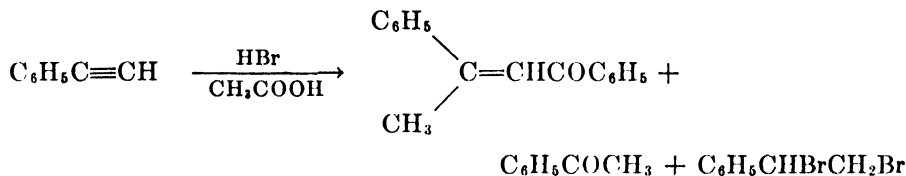
Treatment of styrene oxide with phosphorus pentabromide gave styrene dibromide (743).

As shown in table 14 a great many nuclear-substituted styrenes have been characterized as their dibromides.

The o- (158), m- (158), and p-divinylbenzenes (342, 445) all add two molecules of bromine to give the corresponding tetrabromides. v. Braun and Engel (112) reduced 5-methyl-1,3-phenylenediacetonitrile with sodium in alcohol and pyrolyzed the quaternary methylammonium hydroxide obtained from the resulting amine. The unsaturated hydrocarbon thus produced added bromine.

p-Methylstyrene dibromide also has been prepared by brominating p-methyl-α-bromoethylbenzene in the dark (662). In the presence of light the product was p-methyl-α,α-dibromoethylbenzene. Similarly, both o- and p-bromostyrene dibromides were prepared by brominating the corresponding ethylbenzenes in the absence of light.

p-Methoxystyrene dibromide also has been obtained in 68 per cent yield by allowing anisole and α,β-dibromoethyl ether to stand in glacial acetic acid solution for 5 days (584). The reaction was applied with equal success to phenyl

$$\langle \rangle OCH_3 + C_2H_5OCHBrCH_2Br \xrightarrow[\text{20°C., 5 days}]{CH_3COOH}$$

$$CH_3O\langle \rangle CHBrCH_2Br$$
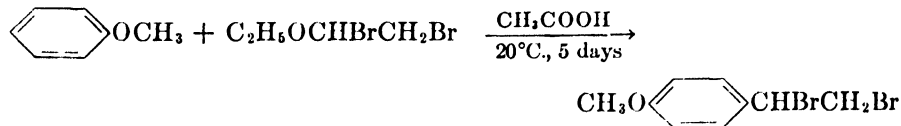
ether, phenoxyacetic acid, and veratrole. In all three cases the dibromoethyl group appeared in the position para to the functional group already present, and in phenyl ether two dibromoethyl groups were introduced.

In the case of 3,4-methylenedioxystyrene dibromide further treatment with bromine introduced a third bromine atom (549).

When vinylphenols are treated with bromine, not only does bromine add to

TABLE 14
Substituted styrene dibromides

SUBSTITUTED STYRENE	REFERENCES
m-Methyl	(525, 750)
p-Methyl	(24, 117, 256, 392, 645, 662, 750)
2,5-Dimethyl	(392, 483)
3,5-Dimethyl	(483)
2,4,5-Trimethyl	(391)
o-Ethyl	(246)
p-Ethyl	(256, 392)
Isopropyl	(551)
p-Isopropyl	(392)
p-Fluoro	(229)
Chloro	(544)
p-Chloro	(215)
3,5-Dichloro	(482)
2,3,4,5,6-Pentachloro	(341, 446)
Bromo	(544)
p-Bromo	(579, 662, 809)
o-Bromomethyl	(110)
o-Nitro	(183)
m-Nitro	(404, 567)
p-Nitro	(56, 283, 317, 404)
2-Nitro-4-isopropyl	(185)
p-Dimethylamino	(111)
o-Dimethylaminomethyl	(188, 217)
m-Cyano	(778b)
m-Carboxy	(404)
o-Methoxy	(586)
m-Methoxy	(234)
p-Methoxy	(551, 742, 758)
3-Nitro-4-methoxy	(184)
p-Phenoxy	(234)
3,4-Dimethoxy	(54, 234, 474)
3,4-Methylenedioxy	(54, 474, 549)
3,4-Carbonyldioxy	(548, 549)
3-Methoxy-4-acetoxy	(619)

the double bond, but the reactive positions in the ring also are substituted. Thus, treatment of o-vinylphenol yielded 2-hydroxy-3,5-dibromostyrene dibromide (247, 248, 686).
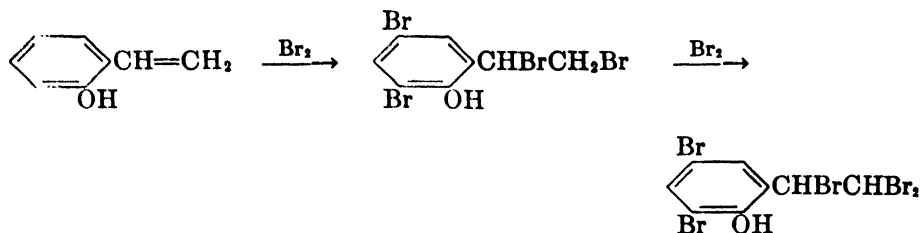
Further treatment with bromine yielded 2-hydroxy-$\alpha,\beta,\beta,3,5$-pentabromo-ethylbenzene. When the reactive 3- and 5-positions were blocked, as in 2-hydroxy-3,5-dimethyl- (6) and 2-hydroxy-3,5-dibromo-styrenes (248), addition proceeded normally to give the corresponding styrene dibromide.

With 3-hydroxy-4-isopropylstyrene a tribromide (probably $\alpha,\beta,2$-tribromo-4-isopropyl-5-hydroxyethylbenzene) was obtained (117). Precipitates also have been observed in the case of 3-hydroxy-4-ethoxy- (359) and 3,4-dihydroxy-styrenes (428).

Treatment of 2,3,5-tribromo-4-hydroxystyrene with bromine yielded the expected styrene dibromide (816). The compound also was prepared in 40–50 per cent yield by treating p-ethylphenol with a large excess of bromine, by brominating the ethyltribromophenol, and by adding hydrogen bromide to the quinoid and normal forms of the corresponding β-bromostyrene.
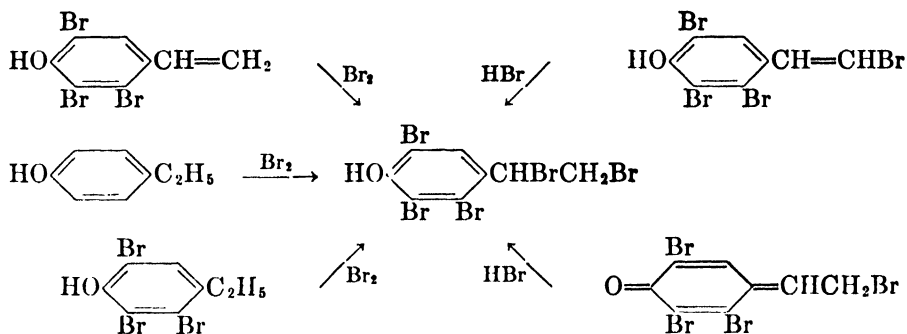
Further bromination of the ethylphenol (75 per cent yield), ethyltribromophenol (70–80 per cent yield), or tribromostyrene dibromide gave $\alpha,\beta,\beta,2,3,5$-hexabromo-4-hydroxyethylbenzene. Bromination of 2,3,5,6-tetrabromo-4-hydroxyethylbenzene gave a low yield of 2,3,5,6-tetrabromo-4-hydroxystyrene dibromide. Under more extreme conditions $\alpha,\beta,\beta,2,3,5,6$-heptabromo-4-hydroxyethylbenzene was obtained in 80–85 per cent yield.

Styrenes substituted in the side chain also add bromine. Dibromides have been obtained from β-chloro- (85, 719), β,β-dichloro- (85), α,β,β-trichloro- (85), and

$$C_6H_5CH{=}CCl_2 + Br_2 \rightarrow C_6H_5CHBrCCl_2Br$$
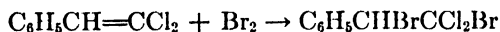
p-bromo-α-chlorostyrenes (173). 3,4-Dimethoxy-β-bromostyrene added bromine quantitatively (474), and bromine addition was observed with $\beta,2,3,5$-tetrabromo-4-hydroxy- and $\beta,2,3,5,6$-pentabromo-4-hydroxy-styrenes (816).

α-Ethoxystyrene reacted instantly with bromine (508), and an unstable dibromide was obtained from β-phenoxystyrene (710). Treatment of α-phenoxy-styrene with bromine gave only tar (635). α-Acetoxystyrene added bromine (479).

Besides β-nitrostyrene itself (199, 200, 571, 737), the substituted β-nitrostyrenes listed in table 15 have been shown to form dibromides.

In the case of 2,4-dimethoxy-β-nitrostyrene the first product isolated was

2,4-dimethoxy-5-bromo-β-nitrostyrene, which then reacted further to form the dibromide (608). .

$$CH_3O\!\!\left<\!\!\bigcirc\!\!\right>\!\!CH\!\!=\!\!CHNO_2 \xrightarrow[\substack{CHCl_3 \\ cold}]{Br_2} CH_3O\!\!\left<\!\!\bigcirc\!\!\right>\!\!CH\!\!=\!\!CHNO_2 \xrightarrow{Br_2}$$

$$CH_3O\!\!\left<\!\!\bigcirc\!\!\right>\!\!CHBrCHBrNO_2$$
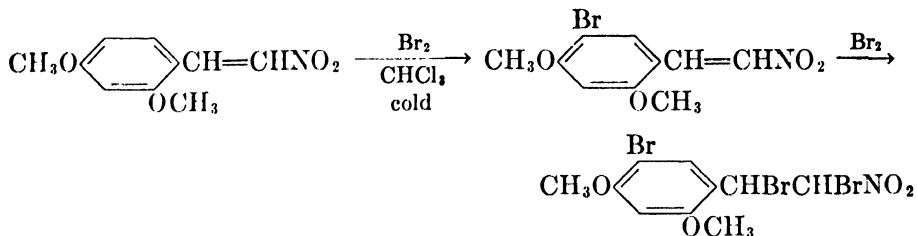
The addition of bromine to β-nitrostyrene was very much slower than the addition of bromine to styrene (749). This reaction also was catalyzed by sulfuric and by hydrobromic acids.

TABLE 15

Dibromides of β-nitrostyrenes

β-NITROSTYRENE	YIELD	REFERENCES
	per cent	
o-Nitro		(45, 571)
m-Nitro		(45)
p-Nitro		(571)
3-Nitro-4-methoxy		(184)
o-Methoxy	90	(608)
p-Methoxy		(608, 627)
3,4-Dimethoxy		(608)
2,3,4-Trimethoxy		(608)
3,4-Methylenedioxy		(530, 608, 627)
p-Methyl		(790)
o-Fluoro		(795)
o-Chloro		(791)
2-Chloro-5-nitro		(791)
2-Bromo-5-nitro		(794)
2-Iodo-5-nitro		(793)

Styrene dibromide has been hydrolyzed to styrene bromohydrin in 59 per cent yield by heating for 6 hr. at 90°C. with an aqueous suspension of calcium carbonate (330). The same reaction has been effected in the case of p-methoxystyrene dibromide (758) and 2,3,5-tribromo-4-hydroxystyrene dibromide (816).

While no bromohydrin was obtained in attempts to hydrolyze 3-methoxy-4-acetoxystyrene dibromide (619), the hydrolysis of 3,4-dimethoxystyrene dibromide (54) by means of aqueous acetone proceeded in nearly quantitative yield (474). The hydrolysis of 3,4-methylenedioxystyrene dibromide similarly was effected (54, 497) in good yield (474). In the case of 3,4-carbonyldioxystyrene dibromide the yield of bromohydrin was 90 per cent (549).

$$O{\overset{\diagup}{\diagdown}}{\underset{OC\diagdown O}{}}\hspace{-1em}\langle\underline{}\rangle CHBrCH_2Br \xrightarrow[\text{acetone}]{H_2O} O{\overset{\diagup}{}}\langle\underline{}\rangle CHOHCH_2Br$$
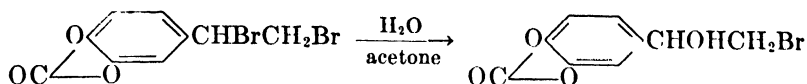
Replacement of the α-bromine atom by alkoxy and acyloxy groups has been effected similarly. Thus, when heated in methanol solution p-methoxystyrene dibromide (584), 3,4-dimethoxystyrene dibromide (474, 584), and 3,4-methyl-

$$CH_3O\langle\underline{}\rangle CHBrCH_2Br \xrightarrow[CH_3OH]{\text{heat}} CH_3O\langle\underline{}\rangle \underset{OCH_3}{CHCH_2Br}$$
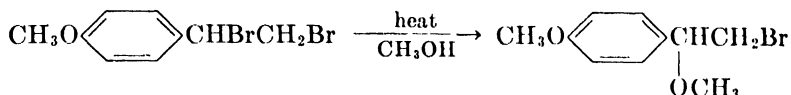
enedioxystyrene dibromide (474) all yielded methyl ethers of the corresponding bromohydrins. The reaction proceeded in the same fashion with 2-hydroxy-3,5-dibromostyrene dibromide (248) and 2,3,5-tribromo-4-hydroxystyrene dibromide (816). The latter bromohydrin ether also was prepared by adding methanol to the quinoid form of the corresponding β-bromostyrene. When o-methoxy-

$$HO\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}CHBrCH_2Br \xrightarrow[CH_3OH]{\text{heat}}$$

$$HO\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}\underset{OCH_3}{CHCH_2Br} \xleftarrow{CH_3OH} O{=}\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}{=}CHCH_2Br$$
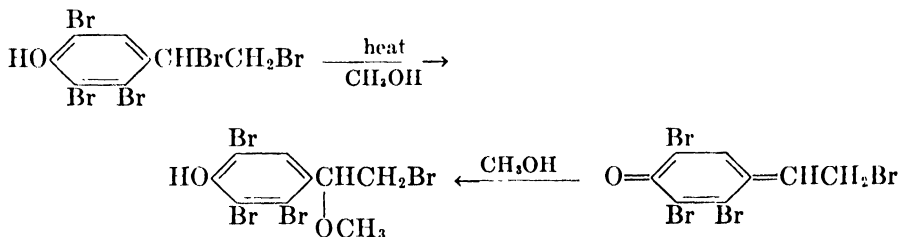
styrene dibromide was treated with an ethanol solution of potassium cyanide, the product was the ethyl ether of o-methoxystyrene bromohydrin (586).

Treatment of 2,3,5-tribromo-4-hydroxystyrene dibromide with sodium acetate in hot acetic acid gave the corresponding bromohydrin acetate (816). Here again the compound was prepared by adding acetic acid to the quinoid form of the corresponding β-bromostyrene.

$$HO\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}CHBrCH_2Br \xrightarrow[CH_3COOH]{CH_3COONa}$$

$$HO\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}\underset{}{\overset{OCOCH_3}{\underset{|}{CH}}CH_2Br} \xleftarrow{CH_3COOH} O{=}\underset{Br\;\;Br}{\overset{Br}{\langle\underline{}\rangle}}{=}CHCH_2Br$$
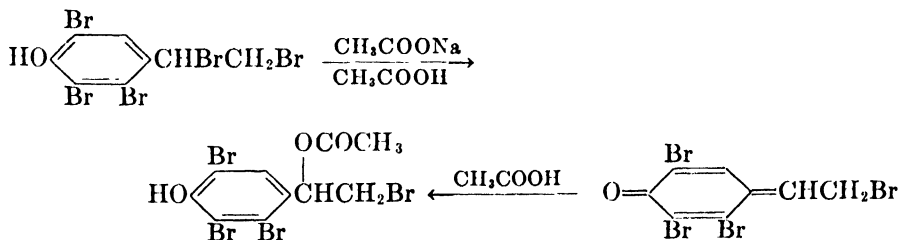
When 2-hydroxy-3,5-dibromostyrene dibromide was heated with sodium acetate and acetic anhydride, not only was the hydroxyl group acetylated, but the α-bromine atom also was replaced by the acetoxyl group (248). Treatment of the same dibromide with sodium acetate and acetic acid gave an acetoxydihydro-coumarone.
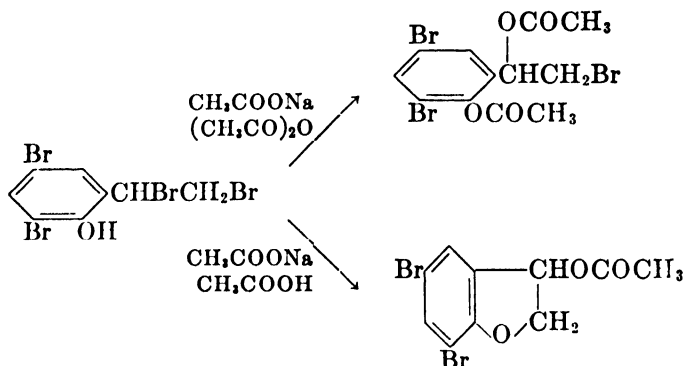
This same type of ring closure has been effected with the bromohydrin ether.

The conversion of both bromine atoms in styrene dibromide to hydroxyl groups has been effected both directly and indirectly by means of a number of reagents. Zincke and Breuer (120, 810, 811) tried a wide variety of combinations, including silver nitrate in acetic acid, potassium acetate in acetic acid, potassium acetate in ethanol, silver benzoate in ethanol, silver acetate in ethanol, silver acetate in acetic acid, silver benzoate in toluene, and aqueous potassium carbonate. In all cases a mixture of styrene glycol, the corresponding ester, α-bromostyrene, and tar was obtained. The combined yield of glycol and ester varied between 5 per cent and 31 per cent except in the case of silver benzoate and toluene, where 50 per cent of styrene glycol dibenzoate was isolated.

Evans and Morgan (214) obtained 47 per cent of styrene glycol by boiling styrene dibromide for 3 days with aqueous potassium carbonate. A 97 per cent yield of the diacetate was produced by treating the dibromide with lead acetate in boiling acetic acid. This diacetate was hydrolyzed to the glycol in 64 per cent yield with dilute sulfuric acid, 74 per cent yield with aqueous calcium carbonate, and 90 per cent yield with aqueous potassium carbonate. This lead acetate-potassium carbonate method has been utilized subsequently (543). p-Bromosty-

$$C_6H_5CHBrCH_2Br \xrightarrow{(CH_3COO)_2Pb} C_6H_5CHCH_2OCOCH_3 \xrightarrow{\underset{H_2O}{K_2CO_3}}$$
$$\underset{\displaystyle OCOCH_3}{|}$$

$$C_6H_5CHOHCH_2OH$$
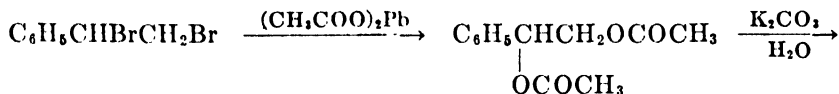
rene dibromide was hydrolyzed to p-bromostyrene glycol by means of aqueous potassium carbonate (662). The bromine in styrene dibromide has been determined by boiling the compound with potassium hydroxide in benzyl alcohol,

diluting with water, and then titrating the halide ion with silver nitrate (647).

In 1845 Blyth and Hofmann (87) observed that treatment of styrene dibromide with alcoholic potassium hydroxide removed a molecule of hydrogen bromide. Subsequently this preparation of α-bromostyrene has been employed by a number of investigators (31, 238, 242, 269, 722, 733) to give yields as high as 85 per

$$C_6H_5CHBrCH_2Br \xrightarrow[C_2H_5OH]{KOH} C_6H_5CBr{=}CH_2$$
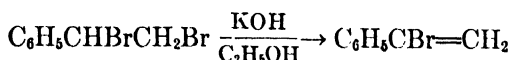
cent (105). Styrene bromohydrin ethyl ether has been observed as a by-product (733). This same reaction has been effected by heating styrene dibromide with water at 190°C. (589).

TABLE 16

Phenylacetylene from styrene dibromide

REAGENT	YIELD	REFERENCE
	per cent	
Sodium amide.....	70	(102)
Potassium hydroxide..	40–50	(102)
Sodium amide...................	40–60	(105)
Sodium amide in toluene.	62	(105)
Sodium amide in kerosene	40	(105)
Sodium amide	64	(763)
Sodium in liquid ammonia	66	(761)
Sodium aniline.............................	45	(90)

When styrene dibromide vapors were passed over calcium oxide at dull red heat, phenylacetylene was obtained (589). This reaction has been effected in fair yield by means of a number of other reagents, as shown in table 16.

$$C_6H_5CHBrCH_2Br \xrightarrow{NaNH_2} C_6H_5C{\equiv}CH$$
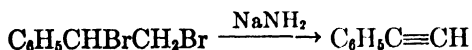
Isopropylstyrene dibromide lost hydrogen bromide on treatment with alcoholic potassium hydroxide to give a bromostyrene (probably α) (551). Under the same conditions m-methylstyrene dibromide gave m-methyl-α-bromostyrene (525). On heating at reduced pressure β-phenoxystyrene dibromide also lost hydrogen bromide, giving a compound postulated as β-bromo-β-phenoxystyrene (710).

Treatment of m- (158) and p-divinylbenzene tetrabromide (445) with alcoholic potassium hydroxide gave m- and p-phenylenediacetylene, respectively. Under the same conditions the ortho isomer gave a variety of products, including naphthalene (158). With sodium ethoxide o-divinylbenzene tetrabromide gave a mixture of o-phenylenediacetylene, o-(α-bromovinyl)phenylacetylene, and o-di(α-bromovinyl)benzene.

In the case of β-nitrostyrene dibromides the α-bromine is removed by alkaline reagents. Priebs (571) originally postulated the β-bromine atom as being removed

by alcoholic sodium hydroxide, but Thiele and Haeckel (737) showed that it was the α-bromine which was removed. The reactions used are given below:

$$C_6H_5CHBrCHBrNO_2 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{CH}_3\text{COONa}} C_6H_5CH{=}CBrNO_2$$

$$\underset{\substack{\nearrow \\ \text{KOH} \\ \text{CH}_3\text{OH}}}{} \qquad \underset{\substack{\searrow \\ \text{KOH} \\ \text{CH}_3\text{OH}}}{\text{boil}}$$

$$\underset{\overset{|}{\text{OCH}_3}}{C_6H_5CHCBr{=}NO_2K} \xrightarrow[\text{H}^+]{} \underset{\overset{|}{\text{OCH}_3}}{C_6H_5CHCHBrNO_2} \quad \underset{\overset{\|}{(\text{OCH}_3)_2}}{C_6H_5CCH_2NO_2}$$

(97 per cent addition) (quantitative)

$$\underset{\substack{\swarrow \\ \text{Br}_2}}{} \qquad\qquad\qquad\qquad \downarrow \text{H}^+$$

$$\underset{\overset{|}{\text{OCH}_3}}{C_6H_5CHCBr_2NO_2} \qquad\qquad C_6H_5COCH_2NO_2$$
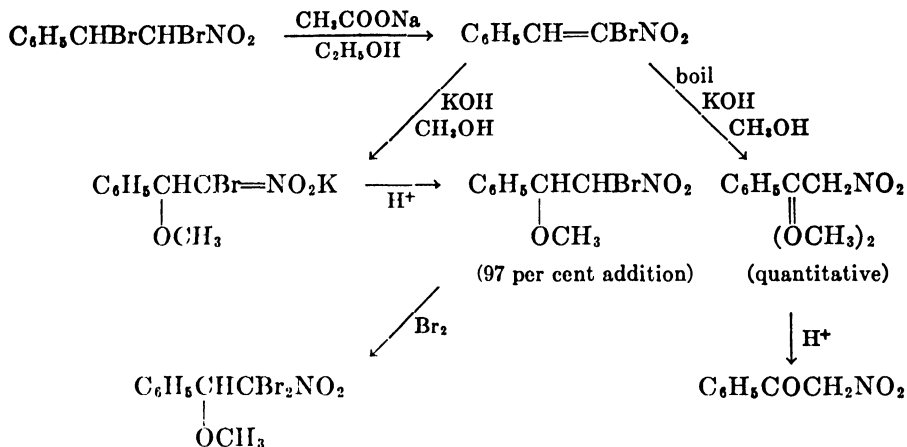
(Since this is alkali-insoluble, both bromine atoms must be on the same carbon atom.)

A parallel series of reactions was conducted with β,p-dinitrostyrene dibromide. An alcoholic solution of sodium or potassium acetate has been used by all subsequent investigators to convert β-nitrostyrene dibromides to β-bromo-β-nitrostyrenes. The compounds listed in table 17 have been prepared in this way. In the case of the 3,4-methylenedioxy compound one group of investigators (530) formulated their product as the α-bromo compound, but this seems unlikely since in every other case the β-compound was produced.

TABLE 17

β-Bromo-β-nitrostyrenes from β-nitrostyrene dibromides

β-BROMO-β-NITROSTYRENE OBTAINED	REFERENCE
o-Methoxy	(608)
p-Methoxy	(608, 627)
3,4-Dimethoxy	(608)
3,4-Methylenedioxy	(530, 608, 627)
2,4-Dimethoxy-5-bromo	(608)
2,3,4-Trimethoxy	(608)
m-Nitro	(45)
p-Nitro	(45)
p-Methyl	(790)
o-Fluoro	(795)
o-Chloro	(791)
2-Chloro-5-nitro	(791)
2-Bromo-5-nitro	(794)
2-Iodo-5-nitro	(793)

Both styrene dibromide (115) and o-ethylstyrene dibromide (246) have been dehalogenated in 70 per cent yield by means of magnesium in ether. With zinc

$$\text{CHBrCH}_2\text{Br} \quad \xrightarrow[\text{ether}]{\text{Mg}} \quad \text{CH=CH}_2$$
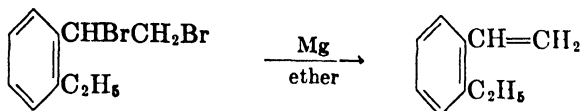
in ether styrene dibromide gave mostly polymer (115). The same reaction is brought about by iodide ion (175), and it has been shown to be first order with respect to both dibromide and iodide-ion concentration (569). Although no reaction occurred in ether at 25°C. (534a), in tetrahydrofuran styrene dibromide reacted with lithium aluminum hydride to give a 71 per cent yield of styrene (756a).

Treatment of styrene dibromide with mercuric cyanide gave a low yield of phenylsuccinonitrile (529). Potassium thiocyanate in boiling alcohol produced styrene dithiocyanate.

$$\begin{array}{c}
\text{Hg(CN)}_2 \nearrow \quad \text{C}_6\text{H}_5\text{CHCH}_2\text{CN} \\
\qquad\qquad\qquad\qquad\quad |\\
\qquad\qquad\qquad\qquad\text{CN}\\
\text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br}\\
\text{KSCN} \searrow \\
\text{C}_2\text{H}_5\text{OH}\\
\qquad\qquad\qquad\text{C}_6\text{H}_5\text{CHCH}_2\text{SCN}\\
\qquad\qquad\qquad\qquad\quad |\\
\qquad\qquad\qquad\qquad\text{SCN}
\end{array}$$
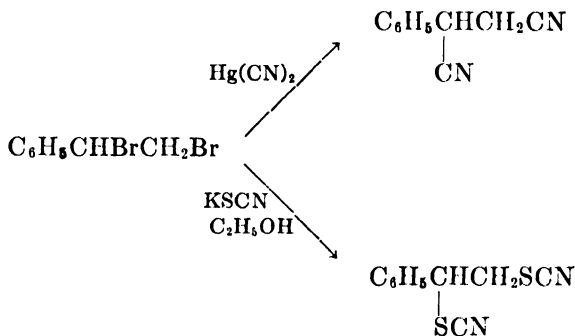
Similarly, sodium sulfite gave disodium ethylbenzene-α,β-disulfonate (377). Alcoholic potassium hydrogen sulfide at 120-130°C. gave a mixture of α,β-dimercaptoethylbenzene and polymeric styrene sulfide (703).

$$\text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br} \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KSH}} (\text{C}_6\text{H}_5\text{CH--CH}_2)_x + \text{C}_6\text{H}_5\text{CHCH}_2\text{SH}$$
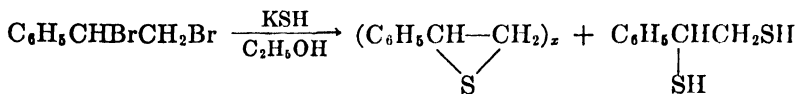
The sodium salt of bis-thioglycolic acid removed hydrogen bromide and gave indefinite products (310). Treatment of styrene dibromide with urea at 120-130°C. gave a product formulated as 2-amino-4-phenyloxazoline (727).

$$\text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br} + \text{H}_2\text{NCONH}_2 \xrightarrow{120-130°\text{C.}} \begin{array}{c}\text{C}_6\text{H}_5\text{CH--N}\\ | \qquad\quad \text{CNH}_2\\ \text{H}_2\text{C---O}\end{array}$$
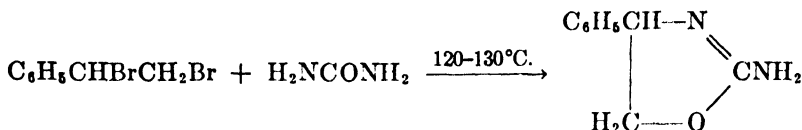
Styrene dibromide did not react with diazoacetic ester (129); with diethylamine at 180°C. it gave a mixture presumably containing both α- and β-diethylamino-

styrenes (63). With benzene and aluminum chloride in carbon disulfide the product was diphenylethane (26).

B. β-Bromostyrene chemistry

Except for the β-nitro-β-bromostyrenes, β-bromostyrenes have not been prepared from styrene dibromides. The routes from cinnamic acid almost invariably have been employed.

In 1863 Schmitt (656) obtained a bromine-containing oil by treating cinnamic acid dibromide with boiling water. In 1864 Erlenmeyer (201) showed that this

TABLE 18

β-Bromostyrene from cinnamic acid dibromide

REAGENT	YIELD OF β-BROMO-STYRENE	BY-PRODUCT	YIELD OF BY-PRODUCT	REFERENCE
	per cent		*per cent*	
Hot water.....		Both bromocin-		(34, 205, 220)
Alcoholic KOH		namic acids		(55)
Aqueous Na₂CO₃	65–75			(8)
Aqueous Na₂CO₃				(34, 168, 171, 292, 450, 522, 717)
Aqueous NaOH				(531)
Alcoholic AgNO₃		Bromocinnamic acid		(444)
Alcoholic CH₃COONa ..				(34)
Alcoholic CH₃COOK . .	92			(713)
Aqueous BaCO₃ .				(717)
Aqueous NH₃..				(717)
Alcoholic dimethylaniline ..		Cinnamic acid		(717)
Aqueous pyridine . .	65–75			(8)
Pyridine	37	Cinnamic acid / α-Bromocinnamic acid	34 / 15	(8)

compound had the empirical formula C_8H_7Br and therefore was a monobromostyrene, for which he suggested the two possible formulas two years later (203). In 1870 Glaser (269) obtained both β-bromostyrene and α-bromo-β-hydroxycinnamic acid from cinnamic acid dibromide and boiling water. He converted the latter product to the former by heating with water at 200°C.

Since these early experiments a number of investigators have used the decomposition of cinnamic acid dibromide for the preparation of β-bromostyrene. The various reagents used are summarized in table 18.

An 81 per cent yield of β-bromostyrene was reported from the bromination of

$$C_6H_5CH{=}CHCOOH \xrightarrow[\text{ether}]{Br_2} C_6H_5CH{=}CHBr$$
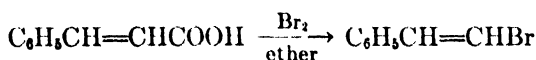
cinnamic acid in ether solution (413). The same product has been reported from bromination in chloroform or carbon tetrachloride (669). Bromination of cinnamic acid in aqueous suspension gave very low yields of β-bromostyrene (596). The principal products were cinnamic acid dibromide (17 per cent) and α-bromo-β-hydroxycinnamic acid (83 per cent) (599). Bromination of aqueous sodium cinnamate gave 5 per cent of cinnamic acid dibromide, 53 per cent of α-bromo-β-hydroxycinnamic acid, and 43 per cent of β-bromostyrene. Later investigators reported somewhat different yields with sodium carbonate present: 49 per cent of α-bromo-β-hydroxycinnamic acid, 5 per cent of cinnamic acid dibromide, and 7 per cent of β-bromostyrene (44).
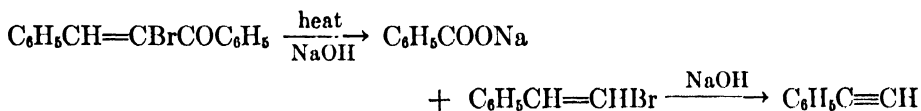
β-Bromostyrene also has been prepared by heating benzalbromoacetophenone with solid sodium hydroxide (168). Some phenylacetylene is obtained in this reaction (171).

$$C_6H_5CH\!=\!CBrCOC_6H_5 \xrightarrow[\text{NaOH}]{\text{heat}} C_6H_5COONa$$
$$+\ C_6H_5CH\!=\!CHBr \xrightarrow{\text{NaOH}} C_6H_5C\!\equiv\!CH$$

Treatment of α-hydroxy-β,β,β-tribromoethylbenzene with zinc and alcohol gave β-bromostyrene (800) as well as some by-product styrene (799).

$$C_6H_5CHOHCBr_3 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Zn}} C_6H_5CH\!=\!CHBr + C_6H_5CH\!=\!CH_2$$
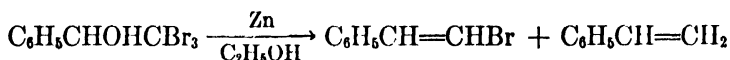
Dufraisse (168, 169, 171) prepared both isomeric forms of β-bromostyrene and studied their properties in detail. He showed that light changed both to an equilibrium mixture containing 90 per cent of the A form. On the basis of physical properties v. Auwers (35) showed that the A and B forms studied by Dufraisse were the *trans* and *cis* forms, respectively.

In general, substituted β-bromostyrenes also have been prepared from the corresponding cinnamic acids. Again the most widely used procedure was to decompose the cinnamic acid dibromide. These preparations are summarized below (table 19).

It is to be noted that Dann, Howard, and Davies (150) obtained different melting points for their *o*-, *m*-, and *p*-nitro-β-bromostyrenes than did Reich and coworkers (600, 601, 603, 604).

Certain substituted β-bromostyrenes have been prepared by the bromination of the corresponding sodium cinnamate. This is true of *m*-methyl- (525), *p*-methyl- in 41 per cent yield (in the presence of sodium hydroxide) (40), and *p*-nitro- (in the presence of sodium carbonate, product mostly α-bromo-β-hydroxy-*p*-nitrocinnamic acid) (44). The 2,4,6-trimethyl homolog was prepared by bromination of the cinnamic acid in carbon disulfide, acetic acid, chloroform, or carbon tetrachloride (88). When *p*-aminocinnamic acid was treated with bromine in acetic acid a *p*-acetaminobromostyrene, which was probably the β-isomer, was obtained (252).

TABLE 19

Preparations of substituted β-bromostyrenes

CINNAMIC ACID DIBROMIDE	DECOMPOSITION REAGENT	YIELD	REFERENCE
		per cent	
p-Bromo	$Na_2CO_3 + H_2O$		(614)
p-Bromo	2% $Na_2CO_3 + H_2O$	70	(615)
p-Bromo (A)*	H_2O		(615)
o-Nitro	$CH_3COONa + H_2O$		(603)
o-Nitro	$CH_3COONa + C_2H_5OH$		(603)
o-Nitro	30% $CH_3COONa + H_2O$	20	(150)
m-Nitro	H_2O	60	(786)
m-Nitro (B)	H_2O	15	(604)
m-Nitro	$Na_2CO_3 + H_2O$		(600, 601)
m-Nitro (C)	$KOH + C_2H_5OH$	A little	(600)
m-Nitro	30% $CH_3COONa + H_2O$	35	(150)
p-Nitro	$CH_3COONa + H_2O$		(603)
p-Nitro	$Na_2CO_3 + H_2O$		(603)
p-Nitro	$CH_3COONa + C_2H_5OH$		(603)
p-Nitro	30% $CH_3COONa + H_2O$	50	(150)
p-Methoxy	30% $KOH + H_2O$		(182)
p-Methoxy	$Na_2CO_3 + H_2O$		(354)
p-Methoxy	$Na_2CO_3 + H_2O$	75	(469)
o-Ethoxy	H_2O		(221)
Bromo-o-methoxy	$CH_3COONa + H_2O$		(552)
2,4-Dimethoxy-5-bromo (D)	$KOH + CH_3OH$	80	(613)
3,4-Methylenedioxy	$CaCO_3 + H_2O$		(218)
3,4-Methylenedioxy	$Na_2CO_3 + H_2O$	90	(469)
3,4-Dibromomethylenedioxy (E)	$KOH + H_2O$		(553)
3,5-Dibromo-4-hydroxy	$KOH + C_2H_5OH$		(814)

* By-products: (A) p-bromobenzaldehyde and p-bromocinnamic acid; (B) m-nitro-α-bromocinnamic acid; (C) m-nitro-α-bromocinnamic acid; (D) β,2,4-trimethoxy-α,5-dibromophenylpropionic acid; (E) the corresponding styrene and both the α- and the β-bromocinnamic acids.

β,2-Dibromo-5-methoxystyrene has been obtained by brominating m-methoxybenzalpyruvic acid in chloroform solution, followed by treatment with potassium acetate in methanol (612).
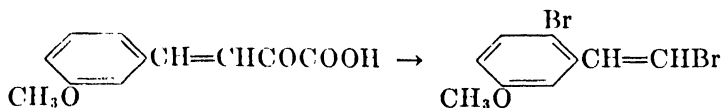
A few β-bromostyrenes have been prepared by distilling the corresponding bromohydrin methyl or ethyl ethers. This is true of o-methoxy- (586), p-methoxy-
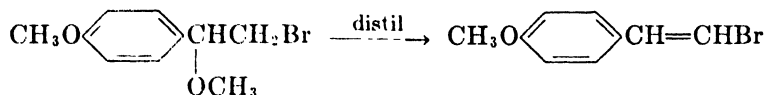
(584), and 3,4-dimethoxy-β-bromostyrenes (474, 584).

$\beta,2,3,5$-Tetrabromo-4-hydroxystyrene was prepared by treating $\alpha,\beta,\beta,2,3,5$-hexabromo-4-hydroxyethylbenzene with zinc and hydrobromic acid in ether (816). The same reaction was used to prepare $\beta,2,3,5,6$-pentabromostyre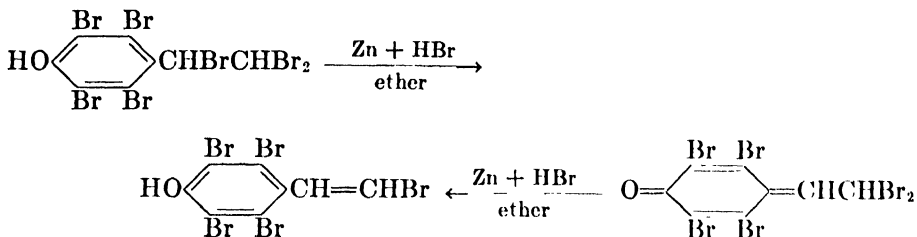ne. This compound also was prepared by treating the quinoid form of $\beta,\beta,2,3,5,6$-hexabromo-4-hydroxystyrene with the same reagent.

β-Bromo-β, p-dinitrostyrene was a by-product obtained in the preparation of α-bromo-p-nitrocinnamic acid by the nitration of α-bromocinnamic acid (560). A mixture of o- and p-nitro-β-bromo-β-nitrostyrenes was obtained by nitrating β-bromostyrene (224).

β-Bromostyrene has served as a convenient source of phenylacetylene. In table 20 are shown the reagents used and the yields obtained.

The same procedures have been used to convert substituted β-bromostyrenes to the corresponding phenylacetylenes. Thus alcoholic potassium hydroxide has been used in the case of p-methoxy-β-bromostyrene (354) with an 84 per cent yield (519) and 3,4-methylenedioxy-β-bromostyrene (218) with a 60.5 per cent yield (469). Sodium amide gave a poor yield of o-methoxyphenylacetylene from o-methoxy-β-bromostyrene (586).

In the experiment marked (A) in table 20 there was obtained as a by-product 17 per cent of β-ethoxystyrene (448, 531). By-product β-methoxystyrene in experiment (B) has been noted above (456). With potassium hydroxide and ethanol at 180°C. the yield of β-ethoxystyrene was nearly quantitative (292).

It has been shown that the hydrolysis of β-bromostyrene by chromic acid and sulfuric acid at 90–95°C. for 2 hr. amounted to 4.3 per cent (117). When heated with water β-bromostyrene yielded phenylacetaldehyde (206).

β-Bromostyrene did not react with sodium malonic ester, sodium acetoacetic ester, or sodium cyanoacetic ester in alcohol, benzene, or xylene (452). It gave a color with antimony trichloride in chloroform (646) and with nitrosyl chloride a nitrosochloride from which hydroxylamine hydrochloride was obtained by heating with hydrochloric acid (556). It did not react with phosphorus pentachloride (68).

Styrylmagnesium bromide and styryllithium, both prepared from β-bromostyrene, have served as agents for the introduction of styryl groups into a large number of compounds. While the Grignard reagent is quite difficult to prepare, it can be made in 90 per cent yield under the proper conditions (267). In this

$$C_6H_5CH{=}CHBr + Mg \xrightarrow{\text{ether}} C_6H_5CH{=}CHMgBr$$
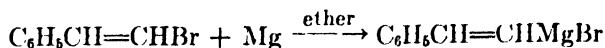
detailed study the other yields varied between 42 per cent and 78 per cent. Because of this yield variation, β-bromostyrene has been used for the evaluation of different forms of magnesium and methods for their activation (262). By-products in the preparation of styrylmagnesium bromide include styrene (509, 740), phenylacetylene (509, 740), and 1,4-diphenylbutadiene (509, 640, 740, 797, 798, 807).

In contrast to p-bromoallyl- and p-bromopropenyl-benzenes, p-bromostyrene was inert to magnesium in ether (578, 580).

TABLE 20

Phenylacetylene from β-bromostyrene

REAGENT	YIELD	REFERENCE
	per cent	
KOH + C_2H_5OH..	40	(305)
KOH + C_2H_5OH, 120–130°C.	18	(531)
Na in ether	24	(531)
KOH + C_2H_5OH, 130–135°C. (A)* ...	60	(531)
KOH + C_2H_5OH....	37	(522)
Na		(740)
KOH + C_2H_5OH, 100°C...	61	(712)
KOH + C_2H_5OH, 125–130°C.	76	(469)
KOH + C_2H_5OH		(168)
KOH + C_2H_5OH		(171)
KOH, 200–215°C.	80	(295)
KOH, 200–230°C. ...	67	(296)
KOH + NaOH, 200–215°C., copper vessel..	70	(641)
CH_3ONa (B)* ..	28	(456)
Na in liquid NH_3	96	(761)
$NaNH_2$ in liquid NH_3	75	(763)
C_6H_5NHNa in ether.	45	(90)
$NaNH_2$ + $C_6H_5NH_2$ (small amount).	89	(90)

* (A) In this experiment 17 per cent of β-ethoxystyrene was obtained as a by-product.

(B) In this experiment there was a 55 per cent recovery of β-bromostyrene and 12 per cent of β-methoxystyrene.

Treatment of styrylmagnesium bromide with water of course gives styrene (640, 798). Carbonation produces cinnamic acid (740, 797, 798) with some phenyl-propiolic acid as a by-product (740). A mixture of the *cis* and *trans* acids was

$$C_6H_5CH{=}CHMgBr \xrightarrow{CO_2} C_6H_5CH{=}CHCOOH + C_6H_5C{\equiv}CCOOH$$
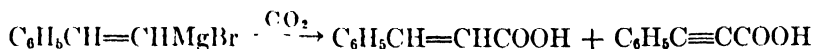
obtained from either the *cis* or the *trans* bromide (797). With acetaldehyde 30 per cent of methylstyrylcarbinol was obtained and with benzophenone 14 per cent of diphenylstryrylcarbinol (509) (isolated as the methyl ether after crystallization from methanol) (714). Other investigators were not able to separate this latter carbinol or the one from methyl p-tolyl ketone from the by-product diphenylbutadiene, but showed their presence by means of the color with concen-

trated sulfuric acid (807). Styrylmagnesium bromide also has been condensed with the following ketones and the resulting carbinols isolated as the perchlorates: p-methoxybenzophenone in 40 per cent yield (807), xanthone in 56 per cent yield (807) (as the chloride in 58 per cent yield) (808), 1-methoxyxanthone (807), and 2,3,5,6-dinaphthalenepyrone (807) in 52 per cent yield (808). Reaction also occurred with estrone acetate (651).

Styrylmagnesium bromide reacted with benzenesulfonyl chloride to give benzenesulfinic acid and β-chlorostyrene (260). Unreacted Grignard reagent was recovered as styrene and some by-product diphenylbutadiene was isolated.

$$C_6H_5CH{=}CHBr \xrightarrow[\text{ether}]{Mg} C_6H_5CH{=}CHMgBr + C_6H_5CH{=}CHCH{=}CHC_6H_5$$

$$\swarrow H_2O \qquad \searrow C_6H_5SO_2Cl$$

$$C_6H_5CH{=}CH_2 \qquad\qquad C_6H_5SO_2H + C_6H_5CH{=}CHCl$$
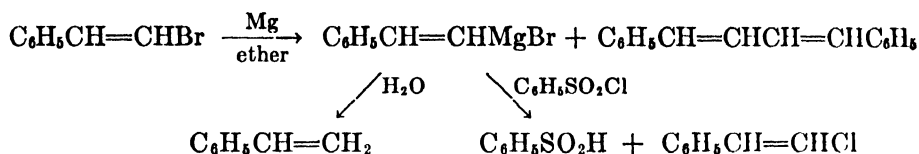
Styrylmagnesium bromide and β-bromostyrene have served as the raw materials for the preparation of a number of organometallic compounds. These reactions are discussed in connection with the various metallic derivatives of styrene.

When β-bromostyrene was treated with lithium in ether 34 per cent of the organo-lithium compound was obtained (266). Since no cinnamic acid was obtained on carbonation, the authors did not believe that they had obtained styryllithium. Subsequently styryllithium was obtained in 68 per cent yield by this method (797). Treatment with water gave principally styrene plus a little phenylacetylene. Carbonation gave cinnamic acid and phenylpropiolic acid in the ratio of four to one. Styryllithium has been added to benzophenone and to distyryl ketone to give the corresponding carbinols (480).

$$\begin{array}{c} C_6H_5CH{=}CHC(C_6H_5)_2OH \\ (43\ \text{per cent}) \end{array}$$

$$(C_6H_5)_2CO \nearrow$$

$$C_6H_5CH{=}CHLi$$

$$(C_6H_5CH{=}CH)_2CO \searrow$$

$$\begin{array}{c} (C_6H_5CH{=}CH)_3COH \\ (33\ \text{per cent}) \end{array}$$
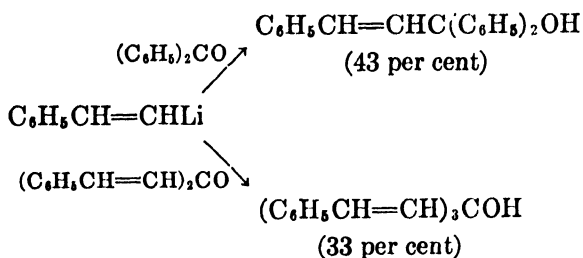
With cholestanone the olefin was obtained (651).

When β-bromostyrene was allowed to stand in petroleum ether for 38 days with butyllithium, the products were 1-phenyl-1-hexene and 1,4-diphenyl-

$$C_6H_5CH{=}CHBr + C_4H_9Li \rightarrow C_6H_5CH{=}CHC_4H_9$$
$$+ C_6H_5CH{=}CHCH{=}CHC_6H_5$$
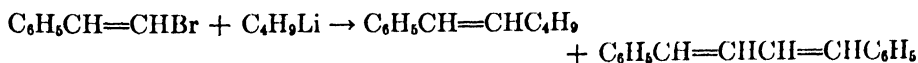
butadiene (478). After boiling in petroleum ether, carbonation of the products of the same reaction yielded 23 per cent of cinnamic acid, 27 per cent of recovered β-bromostyrene, and a trace of phenylbutadiene (263). In ether solution

15 per cent of β-bromostyrene was recovered and the carbonated product was 42.5 per cent of phenylpropiolic acid. When β-bromostyrene was treated with phenyllithium in ether solution and then with benzophenone, 95 per cent of triphenylpropargyl alcohol was produced (782).

$$C_6H_5CH{=}CHBr \quad \xrightarrow[\text{then } (C_6H_5)_2CO]{\text{ether, } C_6H_5Li} \quad (C_6H_5)_2COHC{\equiv}CC_6H_5$$
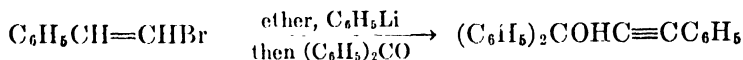
β-Bromostyrene was dehalogenated by lithium aluminum hydride to yield 49 per cent of styrene (756a).

On page 230 are shown several reactions which Thiele and Haeckel (737) conducted with β-bromo-β-nitrostyrene and with β-bromo-β,p-dinitrostyrene. This same conversion of a β-bromo-β-nitrostyrene to an ω-nitroacetophenone has been utilized by other investigators to prepare the following ω-nitroaceto-phenones: m-nitro- (45), p-nitro- (45), o-methoxy- (608), p-methoxy- (608), 3,4-dimethoxy (608), and 3,4-methylenedioxy- (530, 608). The reaction was not applicable to the 2,4-dimethoxy-5-bromo analog. In the case of the o-and p-nitro compounds the mono- and dibromo-ethyl ethers and for the p-nitro compound the mono- and dibromo-methyl ethers (441) also have been prepared (224). For the m-nitro compound the analogous mono- and dibromo-methyl (243, 441) and ethyl (243, 441) ethers have been obtained.
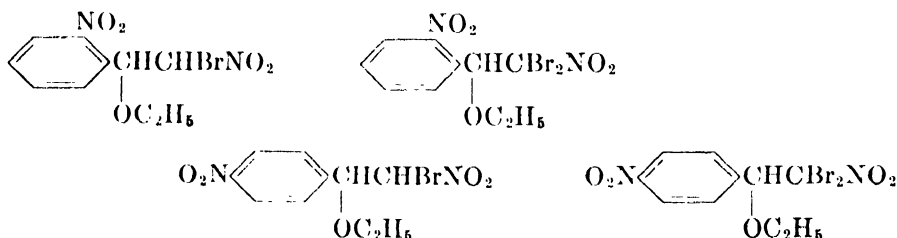
C. α-Bromostyrene chemistry

The preparation of α-bromostyrenes by the dehydrohalogenation of styrene dibromides has already been described. This has been by far the most widely used method of preparation.

α-Bromostyrene has been prepared by adding hydrogen bromide to phenyl-acetylene in glacial acetic acid solution at 0°C. (168, 171, 531). One investigator preferred dry ice temperatures, since at room temperature he obtained primarily dypnone, acetophenone, and a small amount of styrene dibromide (733). The

$$C_6H_5C{\equiv}CH + HBr \quad \xrightarrow{\text{cold}} \quad C_6H_5CBr{=}CH_2 + C_6H_5CBr_2CH_3$$
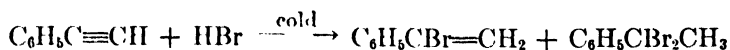
by-product in this reaction is α,α-dibromoethylbenzene, which can be con-verted to α-bromostyrene by means of cold alcoholic potassium hydroxide (531) or by heating with anhydrous ethyl alcohol or with sodium ethoxide in alcohol at 55°C. (733). In the latter case dypnone and acetophenone acetal also were obtained. α-Bromostyrene has been prepared by treating acetophenone with

phosphorus pentabromide. A 68 per cent yield of α-bromostyrene was obtained by treating α,β-dibromo-α-phenethylphosphonic acid with saturated aqueous sodium carbonate at 0°C. (145).

$$C_6H_5CBrCH_2Br \xrightarrow{Na_2CO_3} C_6H_5CBr{=}CH_2$$
$$\overset{|}{PO_3H_2}$$
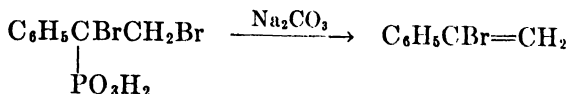
As with β-bromostyrene, α-bromostyrene has served as a source of phenylacetylene. In table 21 are summarized the various reagents which have been used to effect this dehydrohalogenation.

Treatment of phenylacetylene with aqueous hydrogen bromide at 100°C. gave α-bromostyrene and acetophenone in the ratio of two to one (531). α-Bromostyrene has been converted to acetophenone by heating with water (241),

TABLE 21

Phenylacetylene from α-bromostyrene

REAGENT	YIELD	REFERENCE
	per cent	
KOH + C₂H₅OH, 110°C...................		(238)
KOH + C₂H₅OH.............................		(268)
KOH + C₂H₅OH, 120°C...................		(269)
KOH + C₂H₅OH, 130°C......	31	(242)
C₂H₅ONa + C₂H₅OH, 120°C....		(531)
NaNH₂ + kerosene, 160°C......	78	(105)
KOH + C₂H₅OH.............		(168)
KOH + C₂H₅OH...........		(171)

by means of 50–67 per cent sulfuric acid (242), concentrated sulfuric acid (241), and boiling formic acid in 92 per cent yield (31). α-Bromostyrene was not affected by zinc dust in alcohol and gave no sodium phenylacetylide with sodium in ether

$$C_6H_5CBr{=}CH_2 \xrightarrow{HCOOH} C_6H_5COCH_3$$

(431). Swarts (722) stated that treatment with sodium followed by carbonation gave a mixture of cinnamic and phenylpropionic acids. Erlenmeyer (208) later said the reaction yielded a mixture of phenylpropiolic and phenylpropionic acids. Both of these investigators must have obtained some sodium phenylacetylide, in spite of Nef's (531) subsequent statement that no such reaction occurred.

The air oxidation of α-bromostyrene has been mentioned previously. ω-Bromoacetophenone has been isolated as a product of this reaction (170).

D. More highly brominated styrene derivatives

β,β-Dibromostyrene has been prepared by treating α,β,β-tribromoethylbenzene with alcoholic potassium hydroxide (469, 531). Some α,β-dibromostyrene also was isolated from the reaction mixture (531). *m*-Nitro-β,β-dibro-

mostyrene was obtained by heating m-nitro-α,α,β-tribromophenylpropionic acid with aqueous sodium carbonate (601).

$$\text{O}_2\text{N}\langle\text{C}_6\text{H}_4\rangle\text{CHBrCBr}_2\text{COOH} \xrightarrow[\text{H}_2\text{O, Na}_2\text{CO}_3]{\text{heat}} \text{O}_2\text{N}\langle\text{C}_6\text{H}_4\rangle\text{CH}=\text{CBr}_2$$
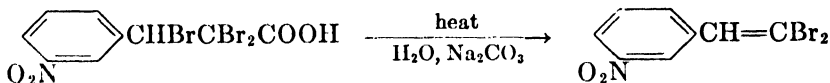
β,β-Dibromostyrene yielded β-bromophenylacetylene on treatment with alcoholic potassium hydroxide (469, 531) and reacted slowly with zinc and alcohol at 100°C. (531). When the vapors of β,β-dibromostyrene were passed over glowing copper, a good yield of phenylacetylene was obtained (531).

α,β-Dibromostyrene has been prepared by treating phenylacetylene with

$$\text{C}_6\text{H}_5\text{C}{\equiv}\text{CH} + \text{Br}_2 \rightarrow \text{C}_6\text{H}_5\text{CBr}{=}\text{CHBr}$$
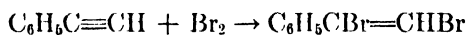
bromine (238; 78 per cent yield, 531) or phosphorus pentabromide (34 per cent yield) (68). Alternate syntheses include treating phenacyl bromide with phosphorus pentabromide (180) or phosphorus dibromotrichloride (some by-product ω,ω-dibromoacetophenone) (732), treating dibromobenzalacetophenone with alkali (167), and heating β-bromo-β-nitrostyrene to 190–200°C. (67 per cent yield)

$$\text{C}_6\text{H}_5\text{COCBr}{=}\text{CBrC}_6\text{H}_5 \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5\text{CBr}{=}\text{CHBr} + \text{C}_6\text{H}_5\text{COOH}$$
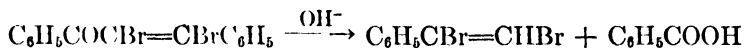
(17). When acetophenone was treated with phosphorus dibromotrichloride, α,β-dibromostyrene was obtained along with phenacyl bromide, ω,ω-dibromoacetophenone, and α,α-dibromoethylbenzene (732).

Treatment of the corresponding phenylacetylene with bromine has been used as a means of preparing the following α,β-dibromostyrenes: p-methyl- (423), p-ethyl- (423), 2-methyl-5-isopropyl- (423), m-nitro- (601), and 2,6-dichloro- (602).

$$\text{H}_3\text{C}\langle\text{C}_6\text{H}_4\rangle\text{C}{\equiv}\text{CH} + \text{Br}_2 \rightarrow \text{H}_3\text{C}\langle\text{C}_6\text{H}_4\rangle\text{CBr}{=}\text{CHBr}$$
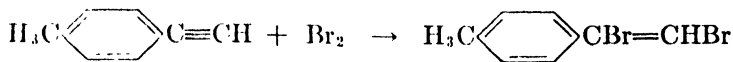
m-Nitro-α,β-dibromostyrene also has been prepared by heating m-nitro-α,β,β-tribromophenylpropionic acid with aqueous sodium carbonate (601).

Treatment of α,β-dibromostyrene with zinc (17) or zinc and alcohol (531) yielded phenylacetylene. Treatment with alcoholic potassium hydroxide yielded primarily β-bromophenylacetylene (531). When α,β-dibromostyrene and 3,4-methylenedioxy-α,β-dibromostyrene were heated with thionyl chloride, chlorinated benzothiophenes were produced (53).

$$\text{C}_6\text{H}_5\text{CBr}{=}\text{CHBr} + \text{SOCl}_2 \xrightarrow{270°C.} [\text{chlorinated benzothiophene}]$$

(70 per cent)
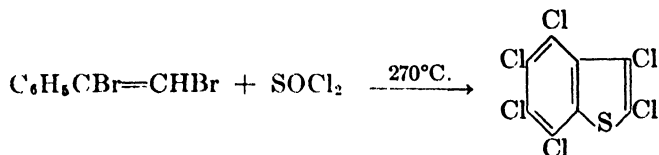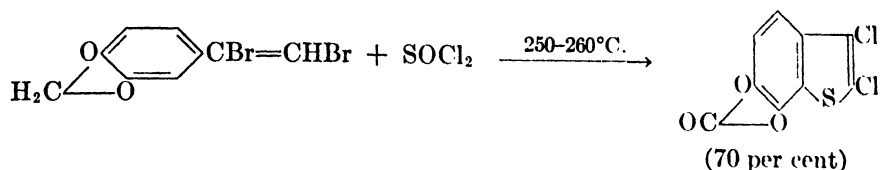
The preparation of α,α-dibromoethylbenzene by the addition of hydrogen bromide to phenylacetylene, together with its conversion to α-bromostyrene, has been described previously. When heated with alcohol or alcoholic potassium hydroxide, α,α-dibromoethylbenzene yielded acetophenone.

Both α,β,β-tribromoethylbenzene (168, 171, 220, 450, 605, 717) and its substituted analogs have been prepared by the addition of bromine to the corresponding β-bromostyrenes. These substituted analogs include o-nitro- (603), p-nitro- (603), o-ethoxy- (221), 2,4-dimethoxy-5-bromo- (613), 3,4-dimethoxy- (474),

$$C_6H_5CH{=}CHBr + Br_2 \rightarrow C_6H_5CHBrCHBr_2$$

3,5-dibromo-4-hydroxy- (814), 2,3,5-tribromo-4-hydroxy- (816), and 2,3,5,6-tetrabromo-4-hydroxy- (816). The last two named also have been prepared by the addition of hydrogen bromide to the quinoid form of the corresponding β,β-dibromostyrene.
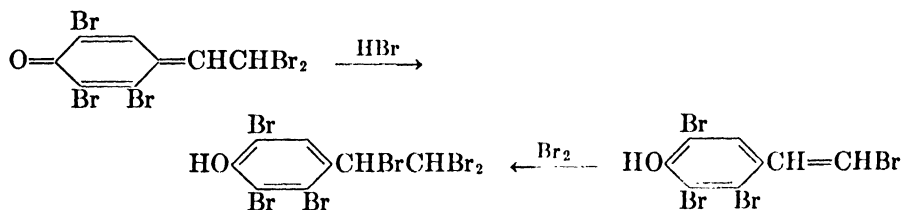
Treatment of α,β,β-tribromoethylbenzene with alcoholic potassium hydroxide yielded mostly β,β-dibromostyrene, together with some α,β-dibromostyrene (531). Treatment with potassium iodide resulted in dehalogenation to give presumably β-bromostyrene (175). α,β,β-Tribromoethylbenzene reacted with benzene in the presence of aluminum chloride to give s-tetraphenylethane (25).

When boiled with potassium hydroxide in methanol or in methanol alone, 2,4-dimethoxy-α,β,β,5-tetrabromoethylbenzene yielded α,2,4-trimethoxy-β,β,5-tribromoethylbenzene (613). Similar results were obtained with ethanol. When
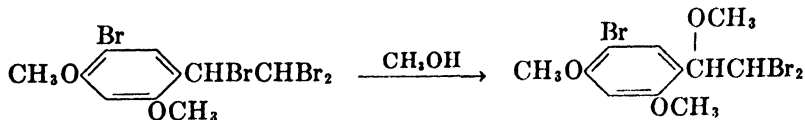
heated in methanol 2-hydroxy-α,β,β,3,5-pentabromoethylbenzene also gave the α-methoxy derivative (248). With α,β,β,3,5-pentabromo-4-hydroxyethylbenzene this same replacement of the α-bromine atom has been effected with methanol and with water and acetone to give the α-methoxy and α-hydroxy derivatives, respectively (814). Both reactions have been conducted successfully

with $\alpha,\beta,\beta,2,3,5$-hexabromo-4-hydroxyethylbenzene and with $\alpha,\beta,\beta,2,3,5,6$-heptabromo-4-hydroxyethylbenzene (816). Treatment of these last two compounds with sodium acetate in acetic acid gave the α-acetoxy derivatives. All six of these last-named substitution products have been prepared by adding the appropriate reagent to the quinoid form of the corresponding β,β-dibromostyrene.
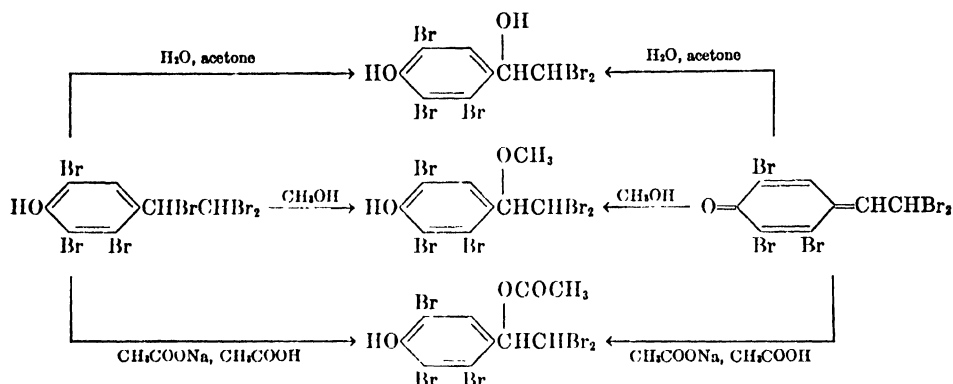
On treatment with zinc and hydrobromic acid in ether $\alpha,\beta,\beta,3,5$-pentabromo-$\alpha,\beta,\beta,2,3,5$-hexabromo-, and $\alpha,\beta,\beta,2,3,5,6$-heptabromo-4-hydroxyethylbenzene all gave the corresponding β-bromostyrenes (814, 816).

α,α,β-Tribromoethylbenzene has been prepared by the addition of bromine to α-bromostyrene (168, 171).

$$\mathrm{C_6H_5CBr{=}CH_2 + Br_2 \rightarrow C_6H_5CBr_2CH_2Br}$$
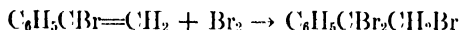
Besides $\alpha,\alpha,\beta,\beta$-tetrabromoethylbenzene itself (180), the following substituted analogs have been prepared by the addition of bromine to the corresponding α,β-dibromostyrenes: p-methyl- (423), p-ethyl- (423), and m-nitro- (601). The o-nitro compound was obtained in 15–20 per cent yield along with 15 per cent of the corresponding cinnamic acid by treating o-nitrophenylpropiolic acid with bromine in acetic acid (289).
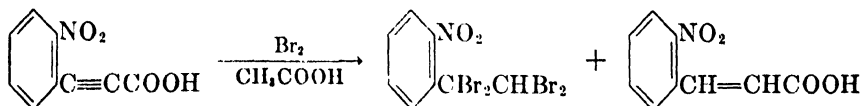
Distillation of $\alpha,\alpha,\beta,\beta$-tetrabromoethylbenzene yielded α,β,β-tribromostyrene (180). m-Nitro-α,β,β-tribromostyrene was prepared by treating the corresponding tetrabromoethylbenzene with alcoholic potassium hydroxide (601). This styrene, which was inert to bromine, was prepared in the same way from m-nitro-α,β,β,β-tetrabromoethylbenzene.
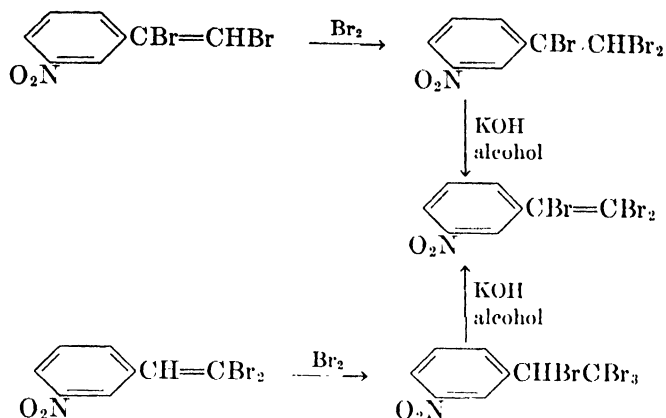
V. MISCELLANEOUS HALOGENATED STYRENE DERIVATIVES

A. Mixed fluoro, chloro, and bromo compounds

Treatment of phenylmagnesium bromide with 1,1-difluoro-2,2-dichloroethane yielded small amounts of β-fluorostyrene, β-chlorostyrene, α-fluoro-β,β dichloroethylbenzene, bromobenzene, and biphenyl (723). Phenylmagnesium bromide and 1,1-difluoro-2,2-dibromoethane yielded mostly bromobenzene and biphenyl, plus small amounts of fluorobenzene and β-fluorostyrene. Treatment of the last-named compound with bromine gave β-fluoro-α,β-dibromoethylbenzene.

When α,α,β,β,β-pentachloroethylbenzene was heated with hydrogen fluoride at 150°C. in a nickel vessel, the product was 65 per cent of difluorotrichloroethylbenzene plus a little α,β,β-trichlorostyrene (772). In an iron vessel the product was 14 per cent of difluorotrichloroethylbenzene and 27 per cent of α,β,β-trichlorostyrene (772, 773).

Treatment of styrene with bromine chloride at −10° to −12°C. gave 65–70 per cent of α-chloro-β-bromoethylbenzene, 20 per cent of styrene dibromide, and 10 per cent of styrene dichloride (759). α-Chloro-β-bromoethylbenzene reacted with alcoholic potassium hydroxide at 0°C. to give 70 per cent of α-chlorostyrene.

$$C_6H_5CHClCH_2Br \xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{KOH}} C_6H_5CCl{=}CH_2$$
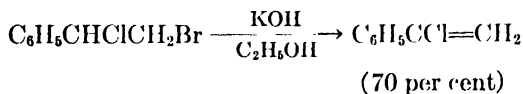
(70 per cent)

p-Methoxy-α-chloro-β-bromoethylbenzene was prepared by treating p-methoxystyrene bromohydrin with acetyl chloride (758). β-Chlorostyrene added bromine

$$CH_3O\langle\ \rangle CHOHCH_2Br + CH_3COCl \rightarrow CH_3O\langle\ \rangle CHClCH_2Br$$
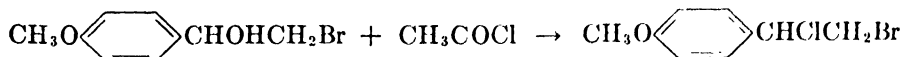
to give 64 per cent of β-chloro-α,β-dibromoethylbenzene in 13 min. (605).

$$C_6H_5CH{=}CHCl + Br_2 \rightarrow C_6H_5CHBrCHClBr$$
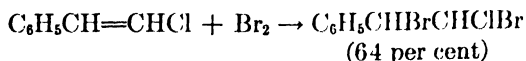
(64 per cent)

3,4-Methylenedioxy-β-chlorostyrene also formed a dibromide (549).

B. Iodinated derivatives

Treatment of styrene with iodine monochloride gave α-chloro-β-iodoethylbenzene (92, 343, 344) in yields as high as 95 per cent (346). This latter compound reacted with water to give styrene iodohydrin (344) and with potassium iodide

$$C_6H_5CH=CH_2 \xrightarrow{\text{ICl}} C_6H_5CHClCH_2I \xrightarrow{\text{H}_2\text{O}} C_6H_5CHOHCH_2I$$
$$\text{(95 per cent)}$$
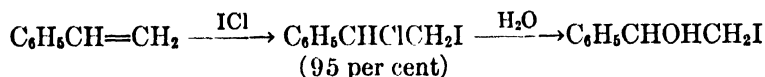
to give styrene, iodine, and potassium chloride (343). With silver nitrate the silver chloride precipitated before the silver iodide.

Berthelot reported that styrene yielded an unstable crystalline iodide on treatment with iodine in potassium iodide (72, 75, 76, 77, 78). The compound decomposed readily to iodine and polystyrene (75, 78). Styrene diiodide has been postulated as the intermediate in the formation of β-phenylnaphthalene from the reaction between hydriodic acid and β-phenoxystyrene or 3-phenyldihydrocoumarone (711).

$$C_6H_5CH=CHOC_6H_5 \xrightarrow{\text{HI}} C_6H_5OH + [C_6H_5CHICH_2I] - $$
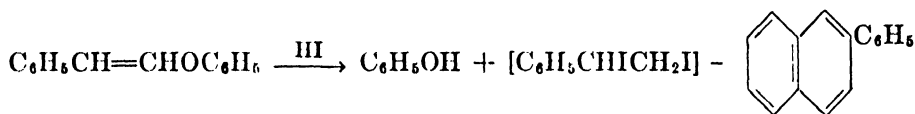
β-Nitrostyrene did not add iodine (571).

When styrylmercuric bromide was treated with iodine in chloroform solution, a 79 per cent yield of β-iodostyrene was obtained (797).

$$C_6H_5CH=CHHgBr \xrightarrow[\text{CHCl}_3]{\text{I}_2} C_6H_5CH=CHI$$
$$\text{(79 per cent)}$$
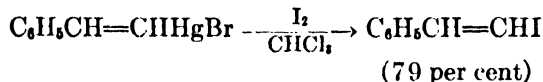
β-Bromophenylacetylene added iodine to give β-bromo-α,β-diiodostyrene (531).

$$C_6H_5C\equiv CBr + I_2 \rightarrow C_6H_5CI=CBrI$$
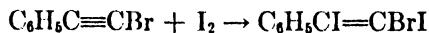
α,β-Diiodostyrene has been prepared by the addition of iodine to phenylacetylene (155, 550) or by the addition of hydrogen iodide to β-iodophenylacetylene (550). With mercurous chloride α,β-diiodostyrene yielded α,β-dichlorostyrene (550).

$$C_6H_5C\equiv CH + I_2$$
$$\searrow$$
$$C_6H_5CI=CHI \xrightarrow{\text{HgCl}} C_6H_5CCl=CHCl$$
$$\nearrow$$
$$C_6H_5C\equiv CI + HI$$
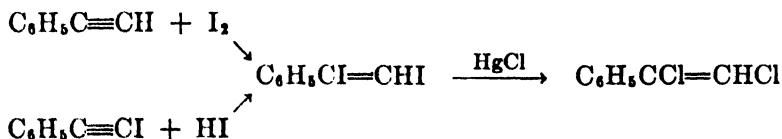
α,β,β-Triiodostyrene has been obtained by a variety of methods such as the reaction between silver phenylacetylide or β-iodophenylacetylene with iodine (451), the reaction between phenylacetylene and nitrogen triiodide (155), and,

along with β-iodo-α-phenylacetylene, from the reaction between silver phenyl-propiolate and iodine in benzene solution (777).

$$C_6H_5C\!\equiv\!CCOOAg \xrightarrow[C_6H_6]{I_2} C_6H_5C\!\equiv\!CI + C_6H_5CI\!=\!CI_2$$
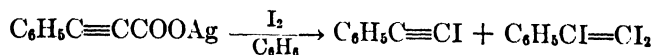
α,β,β-Triiodostyrene and acetophenone were the products obtained by heating α,β-diiodocinnamic acid to 140°C. (550).

VI. STYRENE HALOHYDRIN CHEMISTRY

A. Addition of hypohalous acids

The preparation of styrene halohydrins (defined as β-halo-α-hydroxyethylbenzenes) by the hydrolysis of styrene dihalides, usually by means of a mixture of water and acetone, has been described in detail in connection with the various styrene dihalides.

A number of methods have been adopted to effect the addition of hypochlorous acid to styrene. The earliest (159) utilized chlorourea in acetic acid solution

$$C_6H_5CH\!=\!CH_2 + HOCl \rightarrow C_6H_5CHOHCH_2Cl$$

to give a 95 per cent yield of crude and a 70 per cent yield of pure styrene chlorohydrin. Subsequent investigators (282) were able to obtain only 52 per cent by this method. Other methods included calcium hypochlorite and carbon dioxide (76 per cent yield) (189), sodium hypochlorite and nitric acid (32 per cent yield) (282), and tert-butyl hypochlorite in acetic acid (70 per cent conversion, 84 per cent yield) (282). In the last case omission of the acetic acid led to direct addition of the tert-butyl hypochlorite to the styrene.

$$C_6H_5CH\!=\!CH_2 + (CH_3)_3COCl \rightarrow C_6H_5\underset{\underset{OC(CH_3)_3}{|}}{C}HCH_2Cl$$
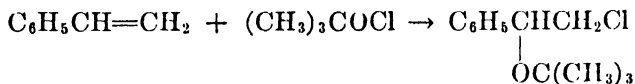
Treatment of styrene with hypochlorous acid in the presence of sodium chloride at 90°C. or sodium carbonate at 40–50°C. gave negligible yields. Styrene chlorohydrin also has been prepared in 58 per cent yield by the reaction between phenylmagnesium bromide and chloroacetaldehyde (697),

$$C_6H_5MgBr + ClCH_2CHO \rightarrow C_6H_5CHOHCH_2Cl$$

and in 86 per cent yield by the reduction of ω-chloroacetophenone with aluminum isopropoxide (260a).

p-Methylstyrene chlorohydrin has been prepared by treating p-methylstyrene with tert-butyl hypochlorite in water or aqueous acetic acid or with chlorourea in aqueous acetic acid (689). When the reaction with tert-butyl hypochlorite was conducted in glacial acetic acid, the product was largely the chlorohydrin acetate. p-Methyl- (696), 3,4-dimethyl- (697), and p-chloro-styrene (65 per cent yield) (696) chlorohydrins all have been prepared by treating the corresponding substituted phenylmagnesium bromide with chloroacetaldehyde. Both 3,4-methyl-enedioxy- and 3,4-carbonyldioxy-styrenes added hypochlorous acid in petroleum

ether and benzene solutions, respectively, to give the corresponding chlorohydrins (549). In the first case the crude product was contaminated with chlorinated chlorohydrin, so that the yield of pure product was only 14 per cent; in the second case the yield was 60 per cent. o-Nitrostyrene chlorohydrin in 49 per cent yield resulted from the addition of hydrogen chloride in pyridine solution to o-nitrostyrene oxide (29).

$$\underset{\substack{\displaystyle \text{CH}-\text{CH}_2 \\ \diagdown \; \diagup \\ \text{O}}}{\overset{\displaystyle \text{NO}_2}{\bigcirc}} \quad \xrightarrow[\text{pyridine}]{\text{HCl}} \quad \underset{\text{CHOHCH}_2\text{Cl}}{\overset{\displaystyle \text{NO}_2}{\bigcirc}}$$
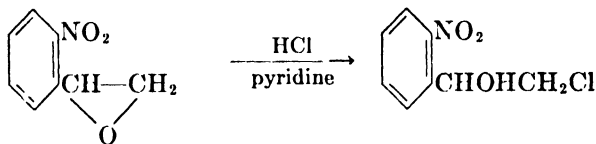
Reduction of o-nitrostyrene chlorohydrin with stannous chloride and hydrochloric acid gave o-aminostyrene chlorohydrin, which yielded a little indole on treatment with alkali (29).

$$\underset{\text{NO}_2}{\bigcirc}\text{CHOHCH}_2\text{Cl} \xrightarrow[\text{HCl}]{\text{SnCl}_2} \underset{\text{NH}_2}{\bigcirc}\text{CHOHCH}_2\text{Cl} \xrightarrow{\text{NaOH}} \underset{\text{H}}{\overset{}{\bigcirc\!\!\!\bigcirc}}_{\text{N}}$$
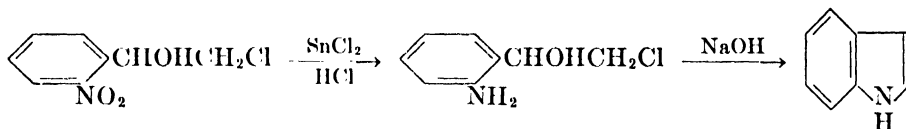
Styrene chlorohydrin has been oxidized to ω-chloroacetophenone by means of potassium dichromate in sulfuric acid (159) in yields as high as 83 per cent

$$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{Cl} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$$
$$\text{(83 per cent)}$$
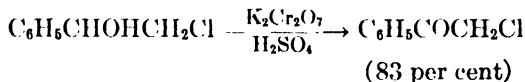
(282). This same oxidation has been effected in the case of o-nitrostyrene chlorohydrin (29).

Treatment of styrene chlorohydrin with acetic anhydride gave a 66 per cent yield of the acetate (282). The p-nitrobenzoate also has been prepared. The acetate of o-nitrostyrene chlorohydrin has been prepared by treating o-nitrostyrene oxide with acetyl chloride in pyridine (29). The benzoate was prepared in the same way, as well as by benzoylation of the chlorohydrin by the Schotten–Baumann method.

When the vapors of styrene chlorohydrin together with steam were passed over an alumina catalyst held at 360–390°C., a 67 per cent yield of acetophenone was obtained (194, 197). Over a silica catalyst impregnated with calcium carbonate, 51 per cent of phenylacetaldehyde contaminated with some β-chlorostyrene was obtained (195, 197).

$$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{Cl} \xrightarrow[\text{CaCO}_3]{\text{H}_2\text{O, SiO}_2} \text{C}_6\text{H}_5\text{CH}_2\text{CHO} + \text{C}_6\text{H}_5\text{CH}\!\!=\!\!\text{CHCl}$$
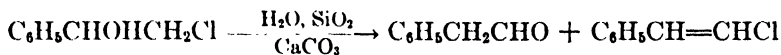
p-Methylstyrene chlorohydrin reacted with 2,4-dimethylphenylmagnesium bromide to give, after boiling with 40 per cent sulfuric acid, a 70 per cent yield of 2,4,4'-trimethylstilbene (696). In the same way a 59 per cent yield of 4-methyl-

$$H_3C\text{—}C_6H_4\text{—}CHOHCH_2Cl + H_3C\text{—}C_6H_4\text{—}MgBr \rightarrow$$

$$H_3C\text{—}C_6H_4\text{—}CH{=}CH\text{—}C_6H_3(CH_3)\text{—}CH_3$$
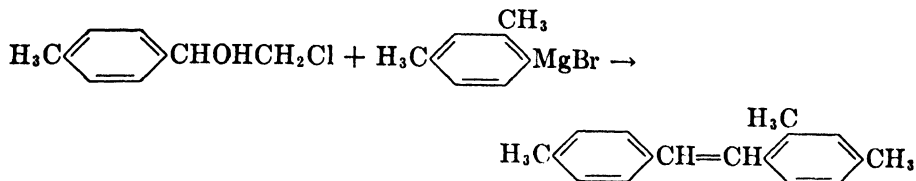
4'-chlorostilbene was obtained from p-chlorostyrene chlorohydrin and p-tolyl-magnesium bromide.

The ethyl ether of styrene chlorohydrin has been obtained by treating phenyl-magnesium bromide with α,β-dichloroethyl ether (744). A yield of 65 per cent has been reported (314).

$$C_6H_5MgBr + C_2H_5OCHClCH_2Cl \rightarrow C_6H_5CHCH_2Cl$$
$$|$$
$$OC_2H_5$$
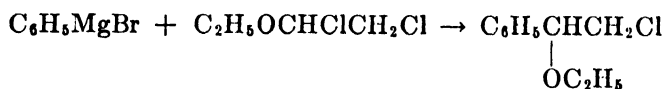
Several investigators have added hypobromous acid to styrene. The best conditions involve the use of bromine water at 90°C. (21, 597, 598, 721), although the only yields given were 91 per cent crude and 55 per cent pure (598). Styrene bromohydrin has been prepared in 90 per cent yield by the reduction of phenacyl bromide with aluminum isopropoxide (461, 462). Reduction with sodium borohydride yielded 71 per cent of styrene bromohydrin (135a).

$$C_6H_5COCH_2Br \xrightarrow[\text{CH}_3\text{CHOHCH}_3]{(i\text{-}C_3H_7O)_3Al} C_6H_5CHOHCH_2Br$$
$$\text{(90 per cent)}$$
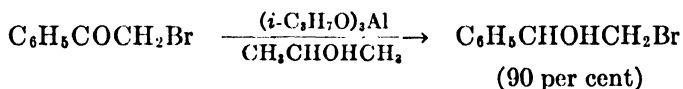
Mixtures of o- and p-ethyl- and o- and p-chloro-styrene bromohydrins have been prepared by treating the corresponding styrene mixtures with hot bromine water (21). In the case of 3,4-methylenedioxystyrene, besides bromohydrin formation, one of the nuclear hydrogens was replaced by bromine (54, 100, 466). The first investigator (466) postulated the reaction as the addition of bromine, but subsequently (54) he was shown to be wrong. In attempts to prepare the bromohydrin of 3-methoxy-4-acetoxystyrene, only tars were obtained when the styrene was treated with hypobromous acid or when the phenacyl bromide was treated with aluminum isopropoxide (619).

α-Bromo-β-hydroxyethylbenzene has been prepared by treating styrene oxide with the magnesium bromide–ether complex (747). It has been characterized as its p-nitrobenzoate and dinitrobenzoate.

$$C_6H_5CH\text{—}CH_2 \xrightarrow[\text{ether}]{MgBr_2} C_6H_5CHBrCH_2OH$$
$$\diagdown\diagup$$
$$O$$
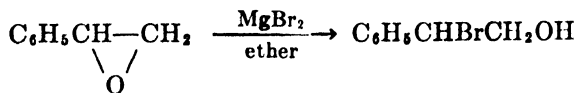
Contrary to the reaction reported with p-methoxystyrene bromohydrin (758), styrene bromohydrin reacted with acetyl chloride to give 91 per cent of the acetate (479). Treatment of 3,5-dibromo-4-hydroxystyrene bromohydrin (814), $\beta,\beta,3,5$-tetrabromo-$\alpha,4$-dihydroxyethylbenzene (814), 2,3,5-tribromo-4-hy-

droxystyrene bromohydrin (816), $\beta,\beta,2,3,5$-pentabromo-$\alpha,4$-dihydroxyethyl-benzene (816), and $\beta,\beta,2,3,5,6$-hexabromo-$\alpha,4$-dihydroxyethylbenzene (816) with acetic anhydride led to the formation of diacetyl derivatives. The preparation of α-acetyl derivatives of the last three named by both acetolysis and addition reactions has been mentioned in connection with the chemistry of the corresponding bromo compounds.

3,4-Methylenedioxystyrene bromohydrin reacted with sulfuryl chloride to give a nuclear-chlorinated analog (100). A similarly brominated 3,4-methylenedioxystyrene bromohydrin was obtained by treating the corresponding styrene with bromine water. Both of these compounds were acetylated with acetic anhydride. In addition the bromo compound underwent the series of reactions shown below.
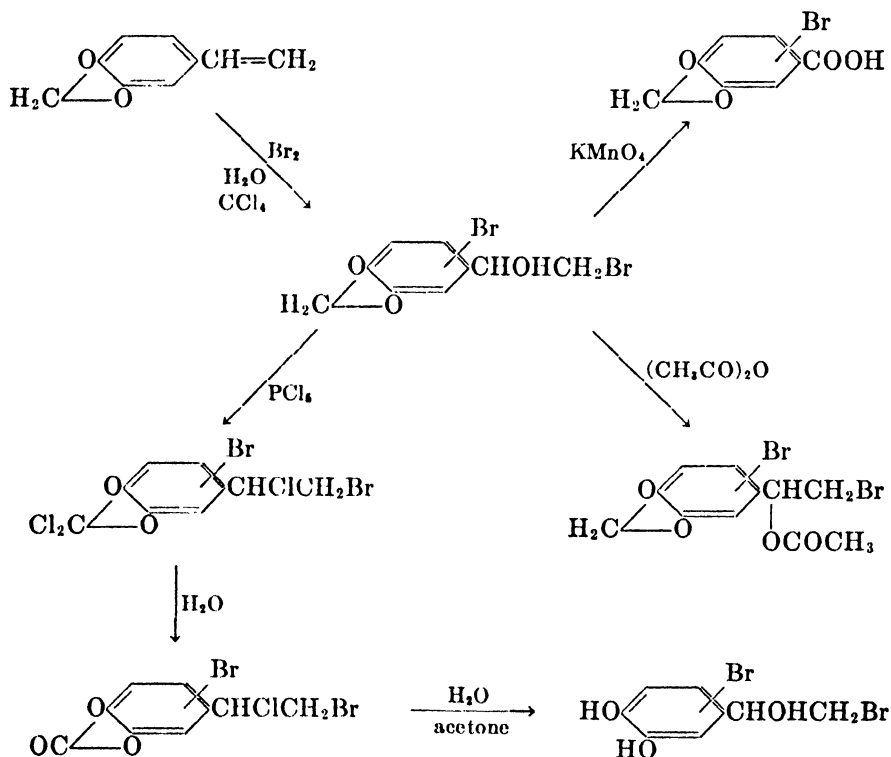
Styrene bromohydrin reacted with sodium sulfite to give sodium β-hydroxy-β-phenylethanesulfonate (377). 3,4-Methylenedioxystyrene bromohydrin gave a benzothiophene derivative on treatment with thionyl chloride at 250–260°C. (53).
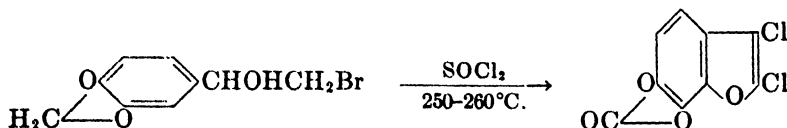
Besides the alcoholysis methods discussed in connection with styrene dibromide and related compounds, β-bromo-α-methoxyethylbenzene has been prepared by treating phenylmagnesium bromide with α-chloro-β-bromoethyl methyl ether (465).

$$C_6H_5MgBr + CH_3OCHClCH_2Br \rightarrow C_6H_5\underset{\underset{OCH_3}{|}}{C}HCH_2Br$$
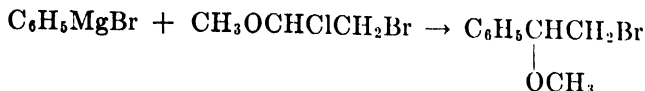
β-Bromo-α-ethoxyethylbenzene has been prepared similarly from phenylmagnesium bromide and α,β-dibromoethyl ether (433) in 90 per cent yield (771) and from phenylmagnesium bromide and β-bromoacetal in 22 per cent yield (696). Treatment of β-phenyl-β-methoxyethylmercuric bromide with bromine in methanol at 0°C. yielded 70 per cent of β-bromo-α-methoxyethylbenzene (796).

β-Bromo-α-ethoxyethylbenzene reacted with a zinc–copper couple in ethanol to give 90 per cent of styrene (771). The same compound gave 74 per cent of

$$C_6H_5\underset{\underset{OC_2H_5}{|}}{C}HCH_2Br \xrightarrow{\text{Zn–Cu}} C_6H_5CH{=}CH_2$$
$$\text{(90 per cent)}$$
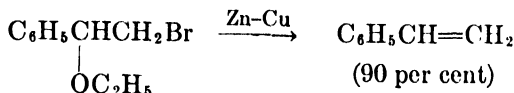
4-methylstilbene when treated with p-tolylmagnesium bromide followed by 40 per cent sulfuric acid (696).

Styrene iodohydrin has been prepared by treating styrene with mercuric oxide, iodine and water (70, 233, 273, 741, 742, 744). The only yield reported was 48

$$C_6H_5CH{=}CH_2 + HgO + I_2 + H_2O \rightarrow C_6H_5CHOHCH_2I$$
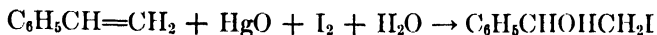
per cent (273). The first investigator to try this reaction reported the product as α-iodo-β-hydroxyethylbenzene (101). Under the same conditions with p-methoxystyrene the intermediate iodohydrin was not isolated and the product isolated was p-methoxyphenylacetaldehyde (742).

On distillation styrene iodohydrin decomposed (101) to acetophenone and hydrogen iodide (741). Treatment with silver nitrate gave phenylacetaldehyde (101, 741, 742).

$$C_6H_5CHOHCH_2I \xrightarrow{\text{AgNO}_3} C_6H_5CH_2CHO$$
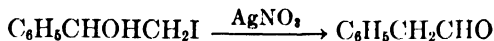
With acetic anhydride the compound was acetylated (742). Styrene iodohydrin reacted with sodium sulfite to give sodium β-phenyl-β-hydroxyethanesulfonate (377) and with methylmagnesium iodide to give β-phenethyl alcohol and a secondary alcohol (273).

Treatment of β-iodo-α-acetoxyethylbenzene with zinc and acetic acid gave α-phenethyl acetate (742).

$$C_6H_5\underset{\underset{OCOCH_3}{|}}{C}HCH_2I \xrightarrow[\text{CH}_3\text{COOH}]{\text{Zn}} C_6H_5\underset{\underset{OCOCH_3}{|}}{C}HCH_3$$
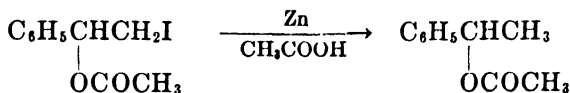
The methyl, ethyl, and amyl ethers of styrene iodohydrin were prepared by treating styrene with mercuric oxide and iodine in the appropriate alcohol (741). The ethyl ether has been prepared by boiling the ethyl ether of styrene chlorohydrin with sodium iodide in ethanol (314).

$$C_6H_5CHCH_2Cl \xrightarrow[C_2H_5OH]{NaI} C_6H_5CHCH_2I$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad OC_2H_5 \quad\quad\quad\quad\quad\quad\quad\quad OC_2H_5$$
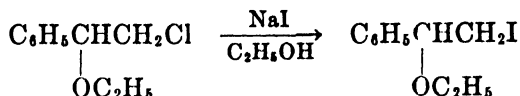
Both the methyl and amyl ethers yield phenylacetaldehyde on treatment with silver nitrate.

α-Iodo-β-hydroxyethylbenzene was obtained by the reaction between styrene oxide and hydriodic acid (273, 742, 744) or magnesium iodide in ether (273, 747). In the latter case if the reaction mixture was hot, phenylacetaldehyde also was

$$C_6H_5CH{-}CH_2 + HI \rightarrow C_6H_5CHICH_2OH$$
$$\qquad\quad\diagdown\diagup$$
$$\qquad\quad O$$
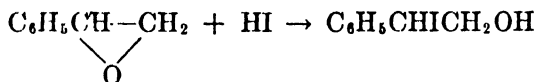
obtained (747). The best yields were 34 per cent with hydriodic acid in ether, 60–85 per cent with hydriodic acid in petroleum ether, and 65 per cent with magnesium iodide in ether (273).

α-Iodo-β-hydroxyethylbenzene has been characterized as its p-nitrobenzoate and dinitrobenzoate (747). With methylmagnesium iodide the products were β-phenethyl alcohol and a secondary alcohol (273). α-Iodo-β-hydroxyethylbenzene reacted with o-aminothiophenol in the presence of alcoholic potassium hydroxide to give 2-phenyldihydrobenzothiazine (148a).

B. Styrene oxide

The preparation of styrene oxide by the epoxidation of styrene has been discussed under that heading. Another common method is to treat a styrene halohydrin with concentrated aqueous alkali or with concentrated alkali in a solvent.

$$C_6H_5CHOHCH_2X \xrightarrow{OH^-} C_6H_5CH{-}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\diagdown\diagup$$
$$\qquad\qquad\qquad\qquad\qquad\qquad O$$
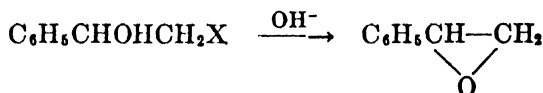
Often the halohydrin is dissolved in a solvent also. These reactions are summarized in table 22.

Other styrene oxides which have been made from the corresponding chlorohydrin and sodium methoxide (697) are p-chloro- (74 per cent yield) and 3,4-dimethyl-. In the latter case considerable 3,4-dimethylstyrene glycol β-methyl ether also was reported. Treatment of o-nitrostyrene chlorohydrin or its acetate with sodium hydroxide gave o-nitrostyrene oxide (29). The method utilizing the bromohydrin and aqueous sodium hydroxide gave a 64 per cent yield of a mixture of o- and p-ethylstyrene oxides and was also used to prepare a mixture of o- and p-chlorostyrene oxides (21).

Impure and partly polymerized d-styrene oxide was obtained along with

acetophenone and styrene glycol by treating d-β-phenyl-β-hydroxyethyltrimethylammonium iodide with water and silver oxide (597). o-Nitrostyrene oxide was prepared by treating o-nitrobenzaldehyde with diazomethane (29, 30). By-products included o-nitroacetophenone and o-nitrophenylacetone (29).

$$
\underset{NO_2}{C_6H_4}CHO + CH_2N_2 \rightarrow \underset{NO_2}{C_6H_4}CH\underset{O}{-}CH_2 +
$$

$$
\underset{NO_2}{C_6H_4}COCH_3 + \underset{NO_2}{C_6H_4}CH_2COCH_3
$$
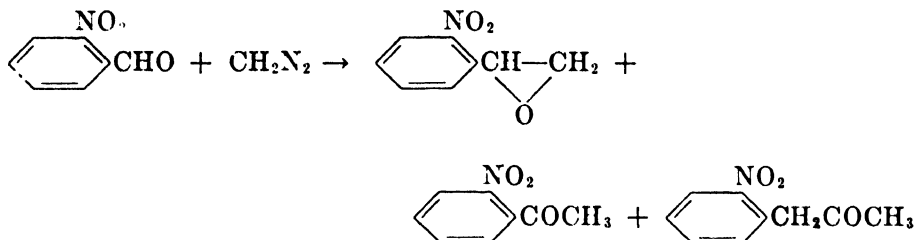
TABLE 22

Styrene oxide from styrene halohydrins

HALOHYDRIN USED	ALKALI	SOLVENTS	TEMPERATURE	YIELD	REFERENCE
			°C.	*per cent*	
Chlorohydrin..	C_2H_5ONa	C_2H_5OH		*	(697)
	KOH	C_2H_5OH		†	(159)
	KOH	H_2O, C_6H_6	42	90	(324, 336)
Bromohydrin ..	NaOH	H_2O	60	73 from styrene	(21)
Iodohydrin...	KOH	None		50 from styrene	(233)
	KOH	None			(741)
	KOH	$(C_2H_5)_2O$		50	(743)
	KOH	$(C_2H_5)_2O$		46 from styrene	(79)
	KOH	$(C_2H_5)_2O$		51 from styrene	(273)

* The product was "mostly" styrene oxide with some by-product styrene glycol β-ethyl ether.

† In this same article it was reported that styrene chlorohydrin and sodium ethoxide gave only β-ethoxy-α-hydroxyethylbenzene.

While no phenylacetaldehyde was obtained when styrene oxide was heated with boiling 20 per cent sulfuric acid or with nitric acid or silver nitrate (742), the aldehyde was obtained when styrene oxide vapors were passed over a metallic catalyst at 200–250°C. (233, 743). Dilute acids gave mostly styrene oxide dimer (743). With such reducing agents as sodium in moist ether (743) or hydrogen and a nickel on calcium carbonate catalyst (322, 337, 455), β-phenethyl alcohol was obtained. In the latter case, besides some recovered oxide, a small amount of phenylacetaldehyde was produced. Reduction of styrene oxide with lithium

aluminum hydride yielded from 75 per cent (756a) to 94 per cent (534a) of α-phenethyl alcohol.

Besides the addition of hydrogen discussed above and that of hydrogen iodide mentioned previously, styrene oxide added hydrogen cyanide to give β-phenyl-β-hydroxypropionitrile (743). With phosphorus pentabromide styrene dibromide

$$C_6H_5CHOHCH_2CN$$

$$C_6H_5CHBrCH_2Br$$
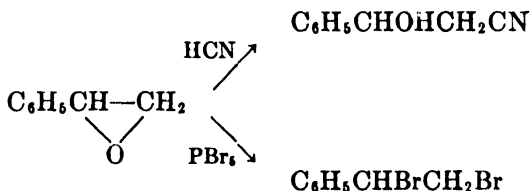
was obtained. Styrene oxide was less reactive toward hydroxylamine than was ethylene oxide (355). With crude pyridine styrene oxide gave a red color after 24 hr. heating at 50–60°C. (457). With pure pyridine the color was brown. Styrene oxide reacted with o-aminothiophenol in the presence of alcoholic potassium hydroxide to give 2-phenyldihydrobenzothiazine (148a).
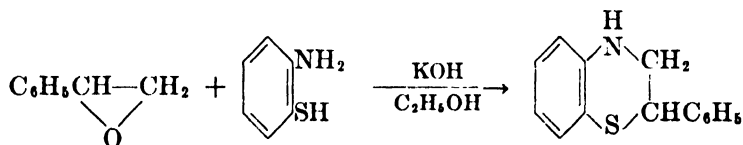
When styrene oxide was added to a solution of phenylmagnesium bromide, an 80–90 per cent yield of β,β-diphenylethyl alcohol was obtained (369). If the addition was reversed, an 80–90 per cent yield of α,β-diphenylethyl alcohol resulted. In each case there was always a trace of the other isomer formed. With methylmagnesium and ethylmagnesium bromides (743) or with methylmagnesium iodide (273), the products were the secondary alcohols. Treatment of styrene oxide with dimethylmagnesium gave a 60 per cent yield of 2-phenyl-1-propanol (273).

Styrene oxide reacted with sodium malonic ester to give a 72 per cent yield of δ-phenyl-δ-butyrolactone (642).
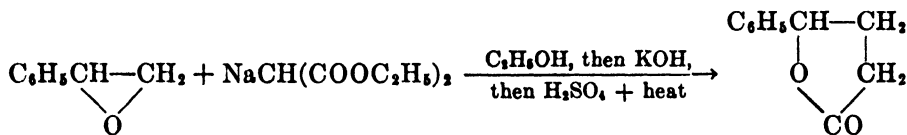
With potassium hydroxide and carbon disulfide the product was 77 per cent of a cyclic trithiocarbonate (149).
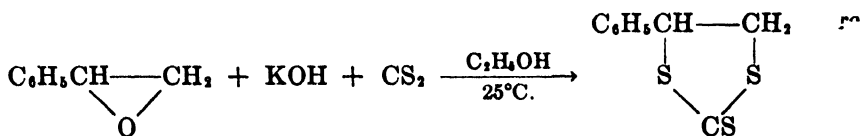
o-Nitrostyrene oxide reacted with formic acid to give 50–75 per cent of *o*-nitroso-ω-hydroxyacetophenone (30).

$$C_6H_4(NO_2)CH\underset{O}{-}CH_2 \xrightarrow{HCOOH} C_6H_4(NO)COCH_2OH$$

With acetic anhydride in the presence of a trace of ferric chloride the acetate was obtained (29). *o*-Nitrostyrene oxide did not react with phenyl isocyanate at 130–140°C., but gave a little indole on treatment with hydrazine hydrate in alcohol.

C. Styrene glycol

The preparation of styrene glycol by the hydrolysis of styrene dichloride or dibromide has been mentioned in connection with the chemistry of those compounds. Styrene chlorohydrin has been hydrolyzed to styrene glycol by boiling with aqueous sodium carbonate (211, 212) or bicarbonate (197).

$$C_6H_5CHOHCH_2Cl \xrightarrow[H_2O]{Na_2CO_3} C_6H_5CHOHCH_2OH$$
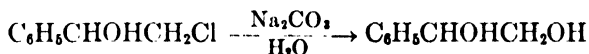
Treatment of styrene with hydrogen peroxide in *tert*-butyl alcohol in the presence of osmium tetroxide yielded 50 per cent of styrene glycol (511). Styrene glycol also has been prepared from styrene by the Prévost reaction (47, 570), in which styrene was treated with silver benzoate and iodine in boiling benzene followed by hydrolysis of the resulting styrene glycol dibenzoate.

$$C_6H_5CH=CH_2 + C_6H_5COOAg + I_2 \longrightarrow$$

$$\underset{\underset{OCOC_6H_5}{|}}{C_6H_5CHCH_2OCOC_6H_5} \longrightarrow C_6H_5CHOHCH_2OH$$
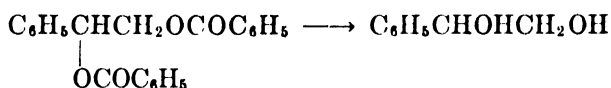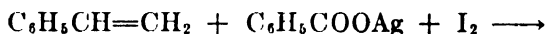
Reduction of ω-hydroxyacetophenone with hydrogen in the presence of Raney nickel gave 85 per cent of styrene glycol (631). Reduction with aluminum amalgam gave styrene glycol and α-phenethyl alcohol (394). A 76 per cent yield was obtained by treating the corresponding acetate with acetone and aluminum isopropoxide followed by hydrolysis with potassium hydroxide (277). Treatment

$$C_6H_5COCH_2OCOCH_3 \xrightarrow[CH_3COCH_3]{(i\text{-}C_3H_7O)_3Al} C_6H_5CHOHCH_2OCOCH_3 \xrightarrow{KOH}$$

$$C_6H_5CHOHCH_2OH$$

of α,β-diacetoxystyrene (from phenacyl bromide and potassium acetate in acetic anhydride) with hydrogen in the presence of platinum oxide gave the diacetate, which was hydrolyzed to styrene glycol with aqueous potassium carbonate (156).

$$C_6H_5COCH_2Br \xrightarrow[\text{(CH}_3CO)_2O]{\text{CH}_3COOK} C_6H_5C{=}CHOCOCH_3 \xrightarrow[\text{PtO}_2]{H_2}$$
$$\overset{|}{O}COCH_3$$

$$C_6H_5CHCH_2OCOCH_3 \xrightarrow[\text{K}_2CO_3]{H_2O} C_6H_5CHOHCH_2OH$$
$$\overset{|}{O}COCH_3$$

In the presence of a palladium catalyst phenylglyoxal and *p*-methylphenyl-glyoxal have been hydrogenated to the corresponding glycols in 71 per cent and 68 per cent yields, respectively (225a).

A 62 per cent yield of styrene glycol was reported to have been obtained by boiling a benzene solution of 2,5-diphenyl-1,4-dioxane with aqueous potassium hydroxide (447). When 2,2-dimethyl-5-phenyloxazolidone was treated with hydrogen in the presence of copper chromite, styrene glycol was one of the products (161).

$$C_6H_5CH{-\!\!-\!\!-}CO$$

$$\underset{H_3C\diagup \,\,\, \diagdown CH_3}{\overset{O\diagdown \,\,\, \diagup NH}{\underset{C}{\diagup \diagdown}}} \xrightarrow[\text{chromite}]{H_2 + \text{copper}}$$

$$C_6H_5CHOHCONH_2 \quad + \quad C_6H_5CHOHCH_2OH$$
$$\text{(35 per cent)} \qquad\qquad \text{(29 per cent)}$$

$$+ \quad C_6H_5CH_2CH_2OH \quad + \quad [(CH_3)_2CH]_2NH$$
$$\text{(3 per cent)} \qquad\qquad \text{(47 per cent)}$$

Styrene glycol was a by-product of the reaction between styrene bromohydrin and sodium sulfite (721) and of the reaction between *d*-(β-phenyl-β-hydroxyethyl)-trimethylammonium iodide and wet silver oxide (597).

Reduction of styrene glycol with hydrogen in the presence of a palladium on charcoal catalyst gave β-phenethyl alcohol and perhaps some ethylbenzene (49).

$$C_6H_5CHOHCH_2OH \xrightarrow{H_2} C_6H_5CH_2CH_2OH$$

Oxidation of styrene glycol with potassium permanganate, potassium ferricyanide, or silver oxide led to nearly quantitative yields of benzoic acid (214). *p*-Bromostyrene glycol behaved similarly with potassium permanganate (662). With lead tetraacetate styrene glycol gave a 78 per cent yield of benzaldehyde (277). The same product was obtained with chromic acid (811). When nitric acid was used as the oxidizing agent, an 80–90 per cent yield of ω-hydroxyacetophenone resulted. The yield was 41 per cent with aqueous bromine and potassium carbonate (214). In this case some benzoic acid also was obtained.

$$C_6H_5CHOHCH_2OH \xrightarrow{HNO_3} C_6H_5COCH_2OH$$
$$\text{(80–90 per cent)}$$

Over platinum in the vapor phase styrene glycol was dehydrogenated to phenyl-glyoxal (757). The electrolytic oxidation gave a large number of products in-

$$C_6H_5CHOHCH_2OH \xrightarrow{\text{Pt}} C_6H_5COCHO$$

cluding benzaldehyde, benzoic acid, mandelic acid, phenylglyoxylic acid, for-maldehyde, and ω-hydroxyacetophenone (753).

Styrene glycol reacted with formic acetic anhydride to give mostly the difor-mate, plus a little of the diacetate (61). With acetyl chloride or acetic anhydride the diacetate was obtained (810, 811). Similar results were obtained with benzoyl chloride and benzoic anhydride (161, 810, 811).

Styrene glycol reacted with phenyl isocyanate to give the diurethan (542). With allophanyl chloride both the β-mono- and the di-allophanate were obtained. Boric acid gave a cyclic borate which was isolated as its potassium salt (291).

$$C_6H_5CHOHCH_2OH + H_3BO_3 \xrightarrow[\text{KOH}]{\text{then}} C_6H_5CH\text{------}CH_2$$
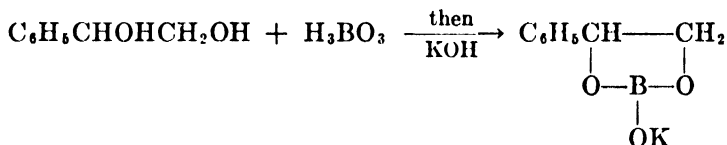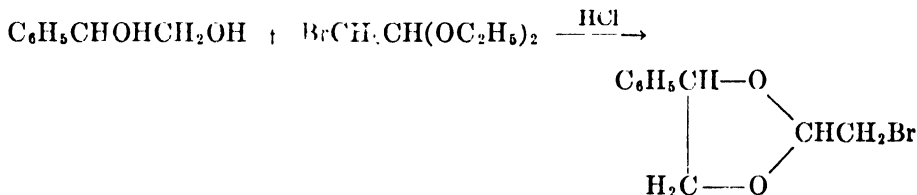
With bromoacetal in the presence of hydrogen chloride a cyclic acetal was pro-duced (232).

$$C_6H_5CHOHCH_2OH + BrCH_2CH(OC_2H_5)_2 \xrightarrow{\text{HCl}}$$

When styrene glycol was heated with potassium hydroxide at 250°C., the products were benzoic acid and 38 per cent of α-phenethyl alcohol (543, 694). With 5 per cent of nickel at 250°C. acetophenone was obtained (281). When styrene glycol vapor together with steam were passed over silica gel impregnated with phosphoric acid, a 74 per cent yield of phenylacetaldehyde resulted (196a, 197). A little aldehyde was obtained in the liquid phase with 15–20 per cent

$$C_6H_5CHOHCH_2OH \xrightarrow[\text{SiO}_2]{\substack{\text{H}_2\text{O} \\ \text{HPO}_3}} C_6H_5CH_2CHO$$
$$\text{(74 per cent)}$$
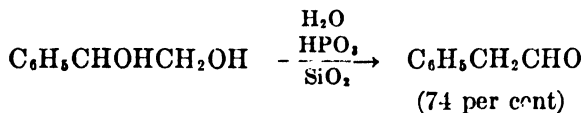
sulfuric acid (120, 811). However, the principal product was β-phenylnaphthalene, which was obtained exclusively when 50 per cent sulfuric acid was used (812, 813) and in yields as high as 60–70 per cent (121). With 48 per cent hydrobromic acid the yield of β-phenylnaphthalene was 78 per cent (135).

$$2C_6H_5CHOHCH_2OH \xrightarrow{\text{heat, H}^+}$$ [structure] C_6H_5
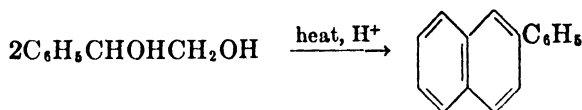
Styrene glycol β-monomethyl ether has been obtained by treating styrene iodohydrin with sodium methoxide or with sodium hydroxide in methanol (741) or by treating styrene chlorohydrin with potassium hydroxide in methanol (61 per cent yield) (189). The β-ethyl ether has been prepared similarly from styrene chlorohydrin and sodium ethoxide (159, 697) or potassium hydroxide in ethanol

$$C_6H_5CHOHCH_2Cl \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}} C_6H_5CHOHCH_2OC_2H_5$$

(65 per cent yield) (189) and from styrene bromohydrin and potassium hydroxide in ethanol (51 per cent yield). The β-n-butyl ether was obtained in 52 per cent yield from the chlorohydrin and potassium hydroxide in 1-butanol.

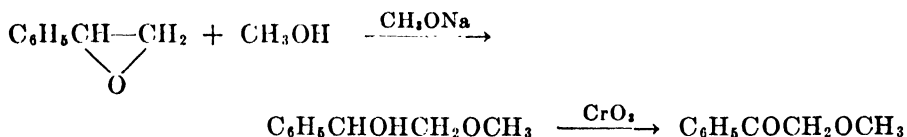When styrene oxide was boiled with an alcohol containing a small amount of phosphoric or sulfuric acid, the corresponding monoether of styrene glycol was formed. By analogy with the above these compounds were formulated as β-ethers, although this structure has since been criticized on theoretical grounds and because hydrogen iodide adds to styrene oxide to give α-iodo-β-hydroxyethylbenzene (358). This method has been used to prepare the monoethyl (47 per cent yield) (189, 738), mono-n-butyl (738) (57 per cent yield) (189), mono-2-ethylhexyl (60 per cent yield) (738), and monolauryl ethers (738). In all cases a by-product, whose analysis indicated it to be a mixture of diphenyldioxanes, also was obtained.

Treatment of styrene oxide with sodium methoxide in methanol gave styrene glycol β-monomethyl ether (358a). The identity of this product was proven by oxidation with chromic acid to ω-methoxyacetophenone. In the case of 3,4-

$$C_6H_5CH\!\!-\!\!CH_2 + CH_3OH \xrightarrow{\text{CH}_3\text{ONa}}$$
$$\underset{O}{\diagdown\diagup}$$

$$C_6H_5CHOHCH_2OCH_3 \xrightarrow{\text{CrO}_3} C_6H_5COCH_2OCH_3$$

diacetoxystyrene the reverse addition occurred, so that the product obtained was 3,4-diacetoxystyrene glycol α-monomethyl ether.

Styrene oxide reacted with allyl alcohol in the presence of sodium to give an 81 per cent yield of a mixture comprising 90 per cent of styrene glycol α-monoallyl ether and 10 per cent of styrene glycol β-monoallyl ether (723a). When sulfuric acid was used as the catalyst, 83 per cent of styrene glycol β-monoallyl ether was obtained. With β-diethylaminoethyl γ-hydroxypropyl sulfide in the presence of potassium hydroxide, 15 per cent of the β-monoalkyl ether was obtained (260a).

By refluxing the appropriate monoether with acetic anhydride containing sodium acetate, acetates of the methyl (189), ethyl (189), n-butyl (189), and diethylaminoethyl (260a) ethers were obtained in yields of 82, 64, 79, and 78 per cent, respectively. Other esters were prepared by refluxing a toluene solution of

the monoether and the acid together with a small amount of p-toluenesulfonic acid (189). The following compounds were prepared in this way in the yields given: caproate of the methyl ether, 55 per cent; butyrate of the ethyl ether, 61 per cent; laurate of the ethyl ether, 32 per cent; benzoate of the butyl ether, 51 per cent.

The diethyl ether of styrene glycol was prepared in 40 per cent yield by treating phenylmagnesium bromide with ethoxyacetal at 100–200°C. (695, 697).

$$C_6H_5MgBr + C_2H_5OCH_2CH(OC_2H_5)_2 \rightarrow C_6H_5\underset{\underset{OC_2H_5}{|}}{CH}CH_2OC_2H_5$$
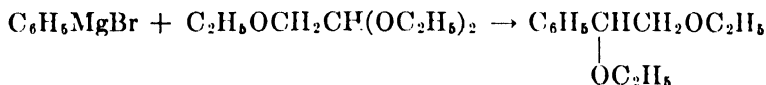
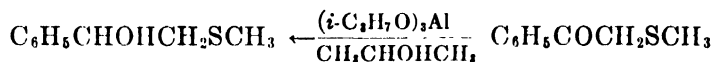By using o-tolylmagnesium iodide, p-tolylmagnesium bromide, 2,4-dimethylphenylmagnesium iodide, and p-chlorophenylmagnesium bromide in the same reaction, the diethyl ethers of the corresponding substituted styrene glycols were obtained (697). The product usually was contaminated with some of the β-ethoxystyrene. All of these diethyl ethers were converted to the corresponding phenylacetaldehydes by boiling with dilute sulfuric acid (695, 697).

Treatment of styrene bromohydrin with sodium methylmercaptide and sodium ethylmercaptide gave 70 per cent and 81 per cent, respectively, of the corresponding β-thioethers of styrene glycol (568). These compounds were prepared in 88 per cent and 58 per cent yields, respectively, by reducing the corresponding ketones with aluminum isopropoxide and isopropyl alcohol.

$$C_6H_5CHOHCH_2Br \xrightarrow{\;NaSCH_3\;}$$

$$C_6H_5CHOHCH_2SCH_3 \xleftarrow[CH_3CHOHCH_3]{(i\text{-}C_3H_7O)_3Al} C_6H_5COCH_2SCH_3$$

This latter method was used to prepare the following substituted styrene glycol β-thioethers in the yields shown: p-methyl methyl, 79 per cent; p-methyl ethyl, 77 per cent; p-methoxy ethyl, 57 per cent; 3,4-dimethoxy methyl, 94 per cent. Styrene bromohydrin also reacted with potassium o-aminothiophenoxide to give the corresponding thioether (148a). In the case of styrene chlorohydrin and sodium β-diethylaminoethylmercaptide, 78 per cent of the β-thioether was obtained (260a). Styrene oxide reacted with the corresponding potassium mercaptides to give the following styrene glycol β-thioethers in the yields specified: methyl, 22 per cent; β-diethylaminoethyl, 20 per cent; γ-diethylaminopropyl, 51 per cent; p-aminophenyl, 68 per cent. With potassium o-aminothiophenoxide, using either styrene oxide or α-iodo-β-phenethyl alcohol, the product was 2-phenyldihydrobenzothiazine (148a).

These compounds behave as typical thioethers, forming quaternary salts with methyl chloride, ethyl chloride, methyl iodide, ethyl iodide, and methyl sulfate. Picrates were prepared by treating the quaternary halides with sodium picrate. The β-ethyl thioether of styrene glycol was oxidized to the sulfoxide by means of hydrogen peroxide. The methyl (311), ethyl (311), phenyl (311), carboxymethyl (310, 311), and carbethoxymethyl dithioethers of styrene glycol have been pre-

pared by treating styrene with the corresponding disulfide in the presence of iodine in anhydrous ether solution.

Styrene glycol β-monoacetate was prepared in 77 per cent yield by reducing ω-acetoxyacetophenone with hydrogen in the presence of a platinum oxide catalyst (671). A little α-phenethyl alcohol also was obtained. The epoxidation of styrene with peracetic acid in acetic acid solution gave styrene glycol or its acetate as the final product of the reaction (97). Styrene oxide was the intermediate.
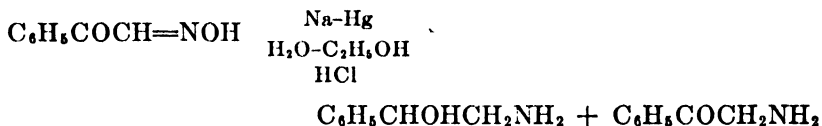
As mentioned previously, styrene glycol diacetate and dibenzoate have been prepared from styrene dibromide. The dipropionate, di-n-butyrate, and dilaurate have been prepared by treating styrene oxide with an excess of the corresponding acid in boiling toluene containing p-toluenesulfonic acid (189).
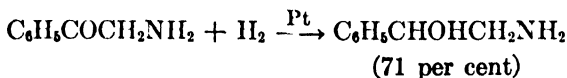
D. Phenylethanolamines

Because of their importance as pressor amines (19), phenylethanolamines (α-hydroxy-β-aminoethylbenzenes) have been studied in great detail, particularly with respect to various methods of synthesis.

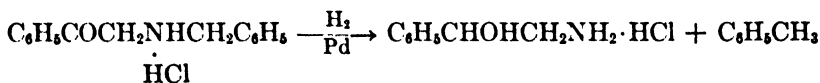$$\langle\!\langle\text{ }\rangle\!\rangle\text{CHOHCH}_2\text{NH}_2$$

For phenylethanolamine itself the most widely investigated methods of preparation have involved reduction. In 1904 Kolshorn (402) first prepared the compound by reducing the monoxime of phenylglyoxal with sodium amalgam in aqueous alcohol containing hydrochloric acid. Some ω-aminoacetophenone was obtained as a by-product.

$$\text{C}_6\text{H}_5\text{COCH}{=}\text{NOH} \quad \xrightarrow[\substack{\text{H}_2\text{O-C}_2\text{H}_5\text{OH} \\ \text{HCl}}]{\text{Na-Hg}}$$

$$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{NH}_2 + \text{C}_6\text{H}_5\text{COCH}_2\text{NH}_2$$

The reduction of ω-aminoacetophenone to phenylethanolamine has been effected in 71 per cent yield in acetic acid solution, using hydrogen in the presence of a

$$\text{C}_6\text{H}_5\text{COCH}_2\text{NH}_2 + \text{H}_2 \xrightarrow{\text{Pt}} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{NH}_2$$
$$\text{(71 per cent)}$$

platinum catalyst (590). The hydrogenation of its hydrochloride (274, 505, 680) or hydrobromide (475) has been effected in alcohol (302) or aqueous solution (475, 505, 680) in the presence of such catalysts as platinum (274) (63 per cent yield), nickel (505), and palladium (475) (28 per cent yield, 680). Phenylethanolamine has been prepared by the reduction of its p-toluenesulfonamide with sodium and amyl alcohol (375). When the hydrochloride of N-benzyl-ω-aminoacetophenone was treated with hydrogen in the presence of a palladium on charcoal catalyst, an 88 per cent yield of phenylethanolamine hydrochloride was obtained (674).

$$\text{C}_6\text{H}_5\text{COCH}_2\text{NHCH}_2\text{C}_6\text{H}_5 \xrightarrow[\text{Pd}]{\text{H}_2} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{NH}_2{\cdot}\text{HCl} + \text{C}_6\text{H}_5\text{CH}_3$$
$$\text{HCl}$$

Another common preparation of phenylethanolamine is by the reduction of mandelonitrile with sodium amalgam in aqueous alcohol using acetic (83,494, 785) or hydrochloric (294) acid to keep the mixture neutral. The yields were low, 26 per cent (83) to 35 per cent (785). However, hydrogenation in alcohol solution using a platinum oxide catalyst in the presence of hydrochloric acid gave only β-phenethylamine (130). Recently a somewhat better yield of phenylethanolamine, 48 per cent, has been obtained by reducing mandelonitrile with lithium aluminum hydride (534a). Benzoyl cyanide has been hydrogenated in acetic acid solution in the presence of a palladium catalyst to give phenylethanolamine (381).
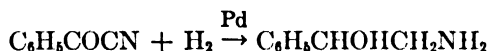
$$C_6H_5COCN + H_2 \xrightarrow{Pd} C_6H_5CHOHCH_2NH_2$$

TABLE 23

Hydrogenation of ω-aminoacetophenones

ω-AMINOACETOPHENONE	CATALYST	YIELD	REFERENCE
		per cent	
p-Methoxy (HCl)	Pd on C		(475)
p-Hydroxy	Pd on C	99	(146)
p-Hydroxy (HCl)	Pd on C		(475)
p-Hydroxy (HCl)	Pd		(381)
p-Hydroxy (HCl)	Pd	89	(674)
3,4-Dihydroxy (HCl)	Pd		(381)
3,4-Dimethoxy (HCl)	Pd		(381)
2-Methoxy-5-methyl	Pt		(117)
2-Hydroxy-5-methyl	Pt		(28)
2,5-Dimethoxy (HBr)	PtO₂		(48)

Treatment of styrene bromohydrin with concentrated aqueous ammonia gave phenylethanolamine (597) in 25 per cent yield (598). Styrene oxide reacted with aqueous ammonia at 90–125°C. to give 18 per cent of phenylethanolamine together with some 2,6-diphenylmorpholine (189).

Phenylethanolamine has been prepared by treating β-hydroxycinnamamide with sodium hypobromite and sodium hydroxide according to the Hofmann procedure (2). Reduction of β-nitro-α-hydroxyethylbenzene with sodium amalgam

$$C_6H_5CHOHCH_2CONH_2 \xrightarrow{NaOBr}{NaOH} C_6H_5CHOHCH_2NH_2$$
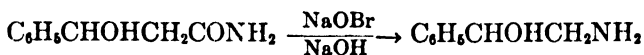
and aqueous alcoholic acetic acid (625, 626) or with iron and sulfuric acid in alcohol (528) also gave phenylethanolamine.

Since the compound is somewhat soluble in water it often has been isolated as a derivative. Those used include the carbonate (83, 475), hydrochloride (2, 597), neutral sulfate (18), picrate (402), and N-benzamide (2, 402, 598).

Nuclear-substituted phenylethanolamines have been prepared almost entirely by procedures involving reduction. The ω-aminoacetophenones listed in table 23 have been hydrogenated to phenylethanolamines. The hydrochloride of 3,4-dichloro-ω-aminoacetophenone has been reduced to the hydrochloride of the

corresponding phenylethanolamine by means of aluminum amalgam (271). 3,4-Dihydroxyphenylethanolamine has been prepared from 3,4-dihydroxy-ω-aminoacetophenone by reduction with sodium amalgam and aqueous sodium hydroxide (493). Reduction of the hydrochloride of N,N-dibenzyl-ω-amino-p-hydroxyacetophenone with hydrogen in the presence of palladium gave an 86 per cent yield of p-hydroxyphenylethanolamine hydrochloride (674).

A number of substituted mandelonitriles have been reduced to the corresponding phenylethanolamines by means of sodium amalgam and acetic acid in alcohol solution. These include p-methyl- (351), p-methoxy- (351), 3,4-methylenedioxy-
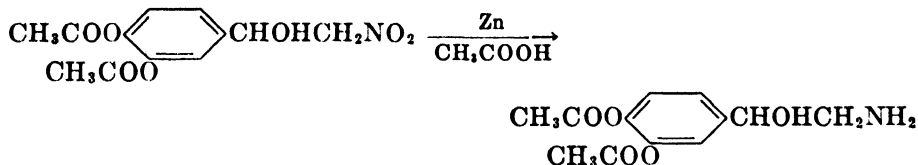
$$H_3C\langle\rangle CHOHCN \xrightarrow{\text{Na-Hg}} H_3C\langle\rangle CHOHCH_2NH_2$$
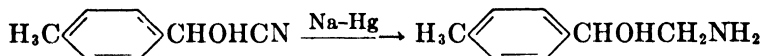
(83, 485), and 3,4-dihydroxy- (494). Hydrogenation in acetic acid solution in the presence of a palladium catalyst likewise has been used successfully for the 3,4-dimethoxy- (47 per cent yield), 3-methoxy-4-ethoxy- (45 per cent yield), and 3,4-diethoxy- (24 per cent yield) substituted analogs (383). In the first two cases 18 per cent and 16 per cent, respectively, of the corresponding β-phenethylamines also were isolated. Hydrogenation in alcohol solution with a platinum oxide catalyst in the presence of hydrochloric acid was successful only in the case of o-methoxy- (59 per cent yield), o-chloro- (41 per cent yield), and 2,3-dimethoxy- (23.5 per cent yield) mandelonitriles (130). In the case of p-chloro- (130), p-methoxy- (130), p-dimethylamino- (130), 3,4-dimethoxy- (130), 3-hydroxy- (130a), 4-hydroxy- (130a), 2-hydroxy-3-methoxy- (130a), 3-methoxy-4-hydroxy- (130a) and 3,4-dihydroxy- (130a) mandelonitriles, only the corresponding β-phenethylamine was obtained. The following benzoyl cyanides have been hydrogenated to phenylethanolamines in acetic acid solution in the presence of a palladium catalyst: p-methoxy-, 3,4-dimethoxy-, 3,4,5-trimethoxy-, and 3,4-methylenedioxy- (381).

α-Hydroxy-β-nitroethylbenzenes have been reduced to phenylethanolamines. Sodium amalgam and acetic acid in alcohol has been used for the following analogs: p-methoxy- (625, 626), 3,4-dimethoxy- (625), and 3,4-dihydroxy- (5 per cent yield) (625). When 3,4-diacetoxy-α-hydroxy-β-nitroethylbenzene was treated with zinc and acetic acid a 49 per cent hield of 3,4-diacetoxyphenylethanolamine was obtained (360).

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\langle\rangle CHOHCH_2NO_2 \xrightarrow[CH_3COOH]{Zn}$$

$$\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\langle\rangle CHOHCH_2NH_2$$

The following ω-nitroacetophenones have been hydrogenated to phenylethanolamines in alcohol solution in the presence of a platinum oxide catalyst: o-methoxy (80 per cent yield), 3,4-dimethoxy- (nearly quantitative yield), and 3,4-methylenedioxy- (80 per cent yield) (608). Hydrogenation of 3,4-dimethoxyphenylglyoxal monoxime in acetic acid solution in the presence of a palladium catalyst gave 65 per cent of the corresponding phenylethanolamine (382).

$$CH_3O\text{—}C_6H_3\text{—}COCH\text{=}NOH + H_2 \xrightarrow{Pd} CH_3O\text{—}C_6H_3\text{—}CHOHCH_2NH_2$$

(65 per cent)
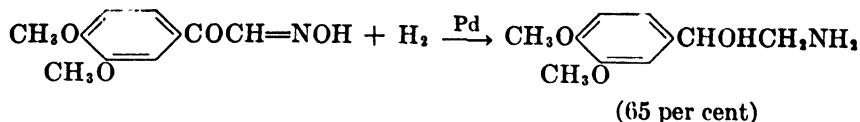
2,5-Dimethoxyphenylethanolamine hydrochloride has been prepared by hydrolyzing the corresponding cyclic urethan with cold concentrated hydrochloric acid (48).

$$\text{(CH}_3\text{O)}_2C_6H_3\text{—CH(—O—CO—NH—)CH}_2 \xrightarrow{HCl} \text{(CH}_3\text{O)}_2C_6H_3\text{CHOHCH}_2NH_2\cdot HCl$$
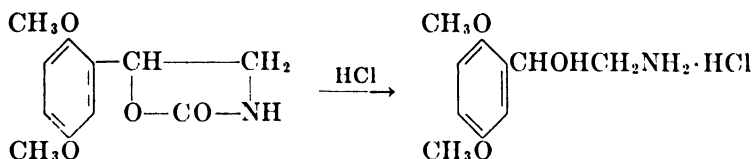
As with phenylethanolamine itself, several derivatives have been utilized for the isolation of substituted phenylethanolamine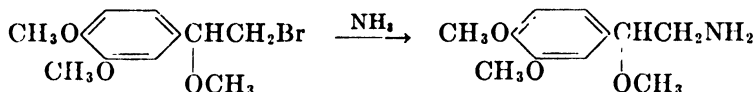s. These include the neutral sulfate for p-methyl-, p-methoxy-, 3,4-dimethoxy-, and 3,4-methylenedioxy- (18); the carbonate for p-hydroxy- (475); and the oxalate for o-methoxy-, 3,4-dimethoxy-, and 3,4-methylenedioxy- (608).

These reductive procedures have been used for the preparation of a number of O-ethers of substituted phenylethanolamines. In table 21 are shown the reducing agents used and the products obtained.

Treatment of the ethyl ether of styrene chlorohydrin with alcoholic ammonia at 90–120°C. gave 9.5 per cent of the ethyl ether of phenylethanolamine plus 18 per cent of the corresponding secondary amine as well as some α-ethoxystyrene (315). α,3,4-Trimethoxyphenylethanolamine has been prepared by treating the corresponding bromo compound with ammonia (474).

$$\text{(CH}_3\text{O)}_2C_6H_3\text{CHCH}_2Br(\text{OCH}_3) \xrightarrow{NH_3} \text{(CH}_3\text{O)}_2C_6H_3\text{CHCH}_2NH_2(\text{OCH}_3)$$
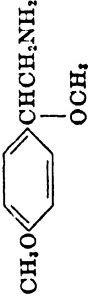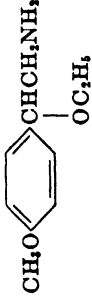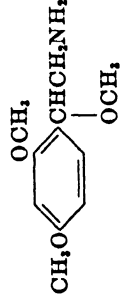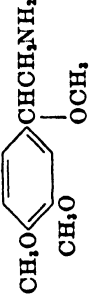
Besides the salts used to isolate phenylethanolamine, the chloroplatinate and neutral oleate also have been prepared (274). Phenylethanolamine is reported to give a very faint blue to blue-green color with sulfomolybdic acid (595). While it was originally reported that phenylethanolamine gave no color when treated with 4 per cent hydrogen peroxide containing sodium chloride (675), a positive test was later observed (286).

In the acylation of phenylethanolamine with acyl halides the first acyl group becomes affixed to the nitrogen atom. This has been shown to be true in the case of the acetyl (785), chloroacetyl (351), benzoyl (83, 381, 475, 597, 674, 726, 785),

$$C_6H_5CHOHCH_2NH_2 + CH_3COCl \rightarrow C_6H_5CHOHCH_2NHCOCH_3$$

and carbethoxy (from ethyl chloroformate) (294, 475) groups. Many N-acyl derivatives also have been prepared by the reduction of the corresponding N-acyl-ω-aminoacetophenones, usually by means of sodium amalgam and aqueous alcohol held neutral with acetic acid. These include the N-formyl (563), N-acetyl (785)

TABLE 24

Reduction of α-hydroxy-β-nitroethylbenzenes

SUBSTITUTED α-HYDROXY-β-NITROETHYLBENZENE	ETHER USED	REDUCING AGENT	PRODUCT	YIELD	REFERENCE
				per cent	
	Methyl	Na–Hg, C_2H_5OH, CH_3COOH	$C_6H_5CHCH_2NH_2$ $\mid$ OCH_3	80	(626)
	Methyl	Electrolysis, Ni cathode	$C_6H_5CHCH_2NH_2$ $\mid$ OCH_3		(626)
	Methyl	Zn, HCOOH	$C_6H_5CHCH_2NH_2$ $\mid$ OCH_3		(476)
p-Methoxy	Methyl	Na–Hg, C_2H_5OH, CH_3COOH	CH_3O—C$_6$H$_4$—$CHCH_2NH_2$ $\mid$ OCH_3		(625, 626)
p-Methoxy	Ethyl	Na–Hg, C_2H_5OH, CH_3COOH	CH_3O—C$_6$H$_4$—$CHCH_2NH_2$ $\mid$ OC_2H_5	80	(625)
2,4-Dimethoxy	Methyl	H_2 + Pt	CH_3O, CH_3O—C$_6$H$_3$—$CHCH_2NH_2$ $\mid$ OCH_3		(471)
3,4-Dimethoxy	Methyl	Na–Hg, C_2H_5OH, CH_3COOH	CH_3O, CH_3O—C$_6$H$_3$—$CHCH_2NH_2$ $\mid$ OCH_3		(625, 628, 628)

			Product	Yield	Ref.
3,4-Dimethoxy	Methyl	Electrolysis, Ni cathode	CH_3O—$C_6H_3(CH_3O)$—CHCH$_2$NH$_2$, OCH$_3$		(626)
3,4-Dimethoxy	Methyl	H_2 + Pd, CH_3COOH	CH_3O—$C_6H_3(CH_3O)$—CHCH$_2$NH$_2$, OCH$_3$	57	(382)
3,4-Dimethoxy	Methyl	H_2 + Pd, CH_3COOH, H_2SO_4	CH_3O—$C_6H_3(CH_3O)$—CH$_2$CH$_2$NH$_2$	50	(382)
3,4-Dimethoxy	Methyl	Zn, HCOOH	CH_3O—$C_6H_3(CH_3O)$—CHCH$_2$NH$_2$, OCH$_3$		(476)
3,4-Methylenedioxy	Methyl	H_2 + Pd, CH_3COOH, H_2SO_4	$H_2C(O_2)C_6H_3$—CH$_2$CH$_2$NH$_2$	50	(382)
3,4-Methylenedioxy	Methyl	Zn, HCOOH	$H_2C(O_2)C_6H_3$—CHCH$_2$NH$_2$, OCH$_3$		(476)
2,5-Dimethoxy-3,4-methylenedioxy	Methyl	H_2 + Pt	$H_2C(O_2)C_6H(OCH_3)(CH_3O)$—CHCH$_2NH_2$, OCH$_3$		(471)
2,5-Dimethoxy-3,4-methylenedioxy	Methyl	Na–Hg, 80% CH_3COOH	$H_2C(O_2)C_6H(OCH_3)(CH_3O)$—CHCH$_2NH_2$, OCH$_3$		(471)

(40 per cent yield) (563), N-benzoyl (785) (58 per cent yield) (563), N-phenacetyl (621) (44 per cent yield) (563), and N-carbethoxy (20 per cent yield) (472). The reduction of N-carbethoxy-ω-aminoacetophenone also has been effected in 75 per cent yield in alcohol solution by means of hydrogen and a palladium catalyst. N-Dichloroacetyl- and N-cyanoacetyl-phenylethanolamines have been

$$C_6H_5COCH_2NHCOOC_2H_5 \xrightarrow[Pd]{H_2} C_6H_5CHOHCH_2NHCOOC_2H_5$$
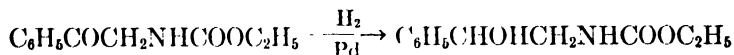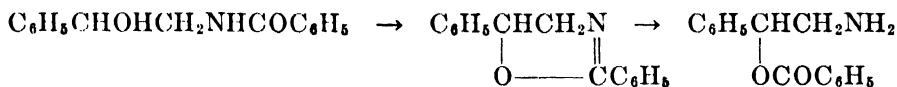
prepared by treating phenylethanolamine with the ethyl ester of the corresponding acid (475). Phenylethanolamine reacted with ethyl chloroacetate to give a diketopiperazine derivative.

$$
2C_6H_5CHOHCH_2NH_2 + 2CH_2ClCOOC_2H_5 \rightarrow
$$
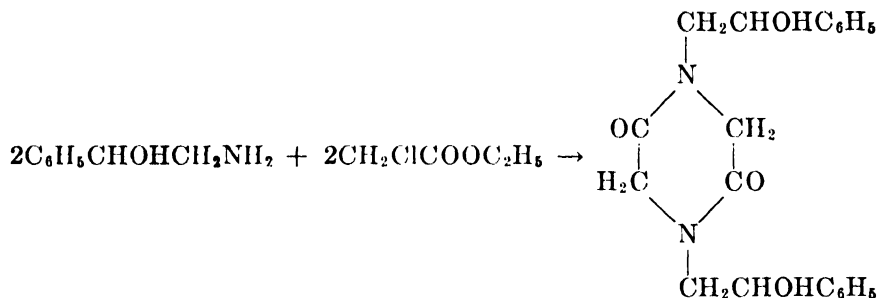
N-Benzoylphenylethanolamine has been acetylated by treatment with acetic anhydride containing sodium acetate (381, 475). When benzoyl chloride and pyridine were used for the benzoylation of phenylethanolamine, instead of benzoyl chloride and sodium hydroxide, the O,N-dibenzoyl derivative was obtained (83).

Treatment of N-benzoylphenylethanolamine with concentrated sulfuric acid, followed by dilution with water and neutralization with potassium carbonate, gave O-benzoylphenylethanolamine sulfate (726). By conducting the neutralization in the cold, the intermediate oxazoline was isolated. O-Benzoylphenyl-

$$C_6H_5CHOHCH_2NHCOC_6H_5 \rightarrow \underset{\underset{O\text{———}CC_6H_5}{}}{C_6H_5CHCH_2N} \rightarrow \underset{\underset{OCOC_6H_5}{}}{C_6H_5CHCH_2NH_2}$$

ethanolamine sulfate reverted to N-benzoylphenylethanolamine on treatment with sodium or ammonium hydroxide.

O-Benzoylphenylethanolamine was obtained along with β-phenethylamine and di(β-phenethyl)amine by the hydrogenation of mandelonitrile benzoate in ethyl acetate solution in the presence of a nickel catalyst (639). Treatment with boiling alcoholic hydrochloric acid gave phenylethanolamine. When N-phenacetyl-phenylethanolamine was treated with concentrated sulfuric acid, no oxazole was obtained and phenylacetaldehyde was isolated from the reaction mixture (621).

Treatment of N-benzoylphenylethanolamine with ethylmagnesium bromide at 175°C. gave N-benzoylstyrylamine (415).

$$C_6H_5CHOHCH_2NHCOC_6H_5 + C_2H_5MgBr \xrightarrow[2\ hr.]{175°C.} C_6H_5CH{=}CHNHCOC_6H_5$$
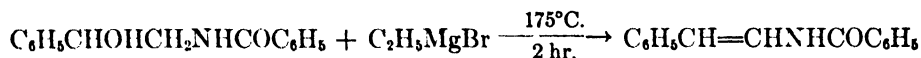
N-Chloroacetylphenylethanolamine added hexamethylenetetramine (351). Neither phenylethanolamine nor N-carbethoxyphenylethanolamine reacted with acetobromoglucose in the presence of silver carbonate (680).

Treatment of N-acetylphenylethanolamine with fuming hydrochloric acid at 100°C. or with phosphorus pentachloride gave N-acetyl-β-chloro-β-phenethylamine (785).

$$C_6H_5CHOHCH_2NHCOCH_3 \xrightarrow[\text{or PCl}_5]{\text{fuming HCl}} C_6H_5CHClCH_2NHCOCH_3$$
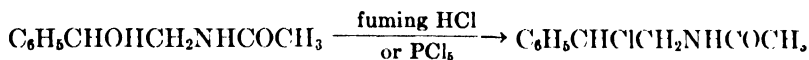
With phenylethanolamine itself the same replacement of the hydroxyl group was effected with hot fuming hydrochloric acid o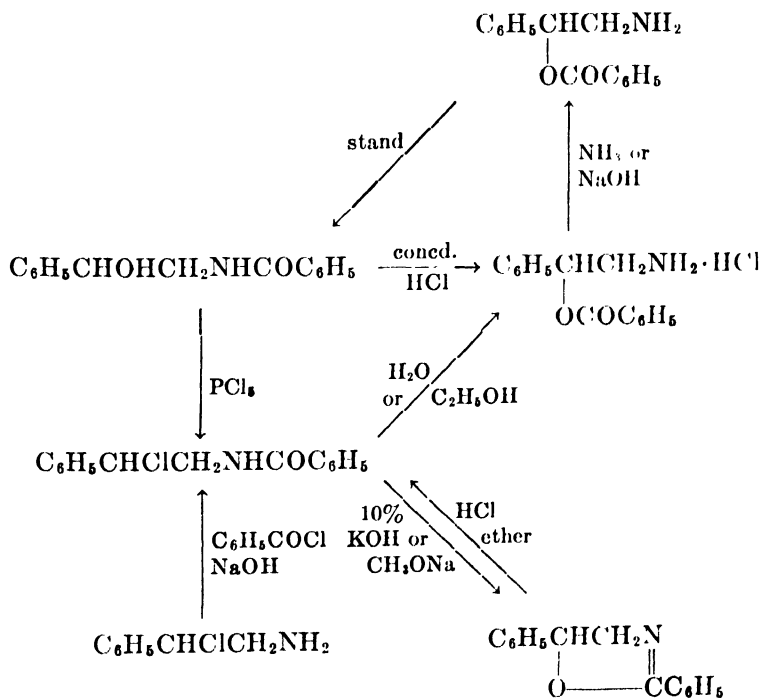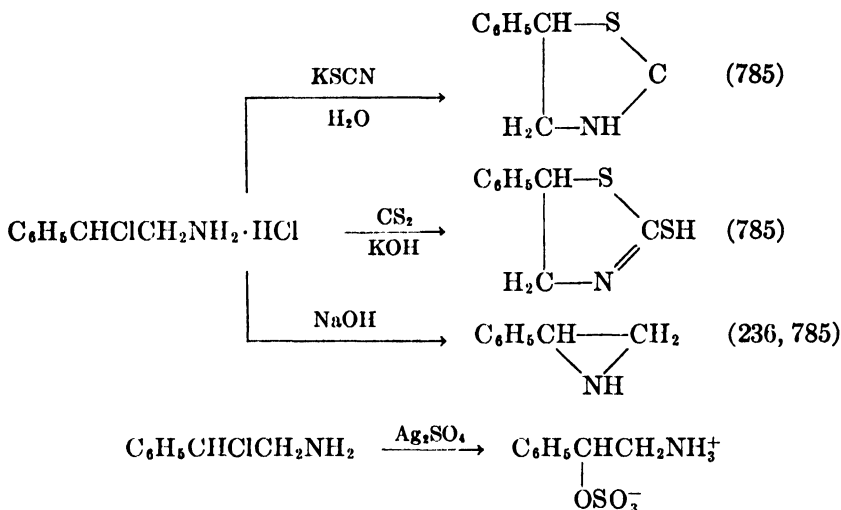r with thionyl chloride. N-Benzoyl-β-chloro-β-phenethylamine was prepared by benzoylating β-chloro-β-phenethylamine by the Schotten–Baumann method (785) or by treating diphenyloxazoline with hydrogen chloride in ether (726). The latter transformation was reversed by 10 per cent potassium hydroxide (726) or sodium methoxide (785). N-Benzoyl-β-chloro-β-phenethylamine was converted to the hydrochloride of O-benzoylphenylethanolamine by treatment with water (726) or hot alcohol (785). This hydrochloride also was obtained by treating N-benzoylphenylethanolamine with hot concentrated hydrochloric acid (726). Treatment of O-benzoylphenylethanolamine hydrochloride with ammonia or sodium hydroxide gave the free amine, which rearranged on standing to N-benzoylphenylethanolamine (785).

$$C_6H_5CHCH_2NH_2$$
$$|$$
$$OCOC_6H_5$$

$$C_6H_5CHOHCH_2NHCOC_6H_5 \xrightarrow[\text{HCl}]{\text{concd.}} C_6H_5CHCH_2NH_2 \cdot HCl$$
$$|$$
$$OCOC_6H_5$$

$$C_6H_5CHClCH_2NHCOC_6H_5$$

$$C_6H_5CHClCH_2NH_2$$

$$C_6H_5CHCH_2N$$
$$| \quad ||$$
$$O———CC_6H_5$$

β-Chloro-β-phenethylamine hydrochloride underwent several interesting reactions which are shown by the following equations:

$$C_6H_5CHClCH_2NH_2\cdot HCl \xrightarrow[H_2O]{KSCN} \begin{array}{c} C_6H_5CH-S \\ | \qquad \diagdown C \\ H_2C-NH \diagup \end{array} \quad (785)$$

$$\xrightarrow[KOH]{CS_2} \begin{array}{c} C_6H_5CH-S \\ | \qquad \diagdown CSH \\ H_2C-N \diagup\!\!\!/ \end{array} \quad (785)$$

$$\xrightarrow{NaOH} \begin{array}{c} C_6H_5CH\!-\!\!-\!\!CH_2 \\ \diagdown NH \diagup \end{array} \quad (236, 785)$$

$$C_6H_5CHClCH_2NH_2 \xrightarrow{Ag_2SO_4} \begin{array}{c} C_6H_5CHCH_2NH_3^+ \\ | \\ OSO_3^- \end{array}$$

A few simple reactions of phenylethylenimine were examined and are also summarized in equation form (785).

$$\begin{array}{c} C_6H_5CH\!-\!\!-\!\!CH_2 \\ \diagdown N \diagup \\ H \end{array}$$

$$\xrightarrow{HCl \text{ or } HBr} C_6H_5CHXCH_2NH_2\cdot HX$$

$$\xrightarrow[H_2O]{HNO_3} C_6H_5CHOHCH_2NH_2\cdot HNO_3$$

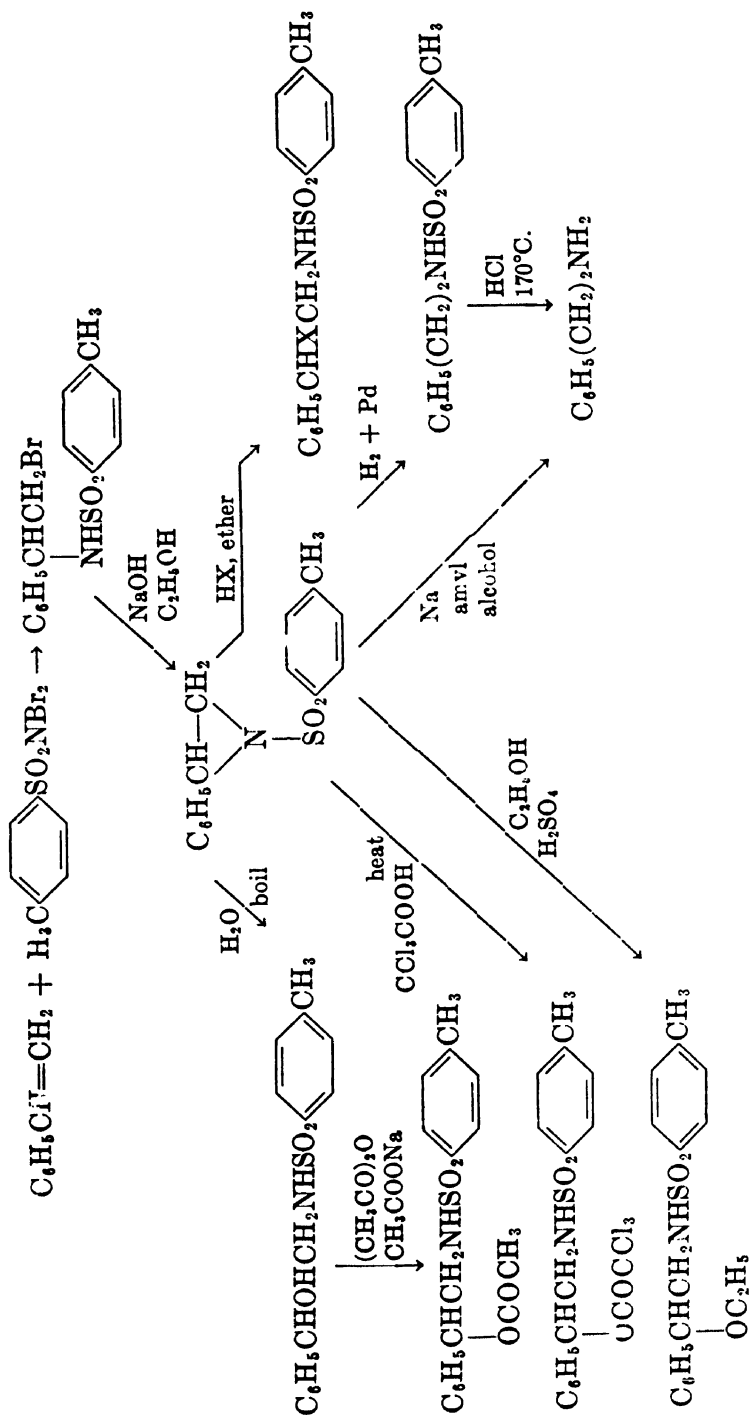$$\xrightarrow[H_2SO_3]{H_2O} C_6H_5CHOHCH_2NH_2\cdot H_2SO_3$$
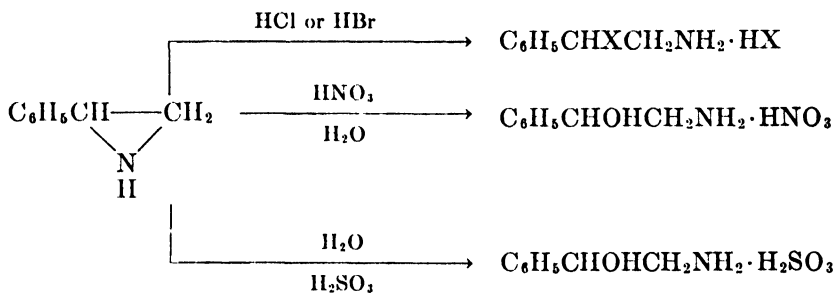
The p-toluenesulfonamide of phenylethylenimine, prepared as shown on page 267, underwent a wide variety of reactions. For convenience these are summarized in equation form (375).

Phenylethanolamine has shown a number of miscellaneous reactions similar to those observed with β-chloro-β-phenethylamine. For convenience they are summarized in equation form (see page 268).

Salts of phenylethanolamine have been prepared with d-camphor-10-sulfonic acid and with d-methylenecamphor, and the d-tartrate has been resolved (597). The d-phenylethanolamine thus formed reacted with methyl iodide and sodium methoxide to give 80 per cent of the d-quaternary iodide (597).

$$C_6H_5CHOHCH_2NH_2 + CH_3I + CH_3ONa \xrightarrow{CH_3OH} C_6H_5CHOHCH_2N(CH_3)_3I$$

$C_6H_5CH=CH_2 + H_2C$⟨ring⟩$SO_2NBr_2 \rightarrow C_6H_5CHCHCH_2Br$

$NHSO_2$⟨ring CH_3⟩

$C_6H_5CH—CH_2$ ⟨ring with N, SO_2, CH_3⟩

NaOH
C_2H_5OH

HX, ether

$C_6H_5CHXCH_2NHSO_2$⟨ring CH_3⟩

$H_2 + Pd$

$C_6H_5(CH_2)_2NHSO_2$⟨ring CH_3⟩

$\xrightarrow[170°C.]{HCl}$

$C_6H_5(CH_2)_2NH_2$

Na
amyl
alcohol

C_2H_5OH
H_2SO_4

H_2O
boil

CCl_3COOH
heat

$C_6H_5CHOHCH_2NHSO_2$⟨ring CH_3⟩

$(CH_3CO)_2O$
CH_3COONa

$C_6H_5CHCH_2NHSO_2$⟨ring CH_3⟩
$OCOCH_3$

$C_6H_5CHCH_2NHSO_2$⟨ring CH_3⟩
$OCOCCl_3$

$C_6H_5CHCH_2NHSO_2$⟨ring CH_3⟩
OC_2H_5

$$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{NH}_2 \xrightarrow[\text{HCl}]{\text{KOCN}} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{NHCONH}_2 \quad (475)$$

$$\xrightarrow{\text{C}_6\text{H}_5\text{NCS}} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{NHCSNHC}_6\text{H}_5 \quad (402)$$

$$\xrightarrow[\text{HBr}]{\text{fuming}}$$

$$\xrightarrow[\text{HN}=\text{C}-\text{NH}_2\cdot\text{HI}]{\overset{\text{SCH}_3}{|}} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{NHC}\overset{\text{NH}}{\underset{\text{NH}_2\cdot\text{HI}}{\diagup}} \quad (83)$$

$$\xrightarrow[\text{C}_6\text{H}_5\text{CHO}]{\text{C}_2\text{H}_5\text{OH}} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{N}=\text{CHC}_6\text{H}_5 \quad (597)$$

$$\xrightarrow{} \text{C}_6\text{H}_5\text{CHOHCH}_2\text{N}=\text{CH} \quad (83)$$

TABLE 25
N-Acylphenylethanolamines

PHENYLETHANOLAMINE	N-SUBSTITUTED DERIVATIVES	REFERENCES
p-Methyl	Chloroacetyl	(351)
p-Methoxy	Benzoyl	(381, 475)
	Carbethoxy	(475)
3,4-Dimethoxy	Homoveratroyl	(381, 562*)
3,4-Methylenedioxy	Formyl	(485)
	Benzoyl	(381, 485)
	p-Nitrobenzoyl	(485)
	Veratroyl	(485)
p-Benzoxy	Benzoyl	(475, 674, 758)

* By reduction of the acylaminoacetophenone with sodium amalgam and acetic acid in alcohol.

A number of nuclear-substituted phenylethanolamines have been acylated by standard methods to give N-substituted derivatives. These compounds are listed in table 25, together with one prepared by another method.

Certain of the above listed N-acyl compounds have been further acylated to give N-acyl-O-acyl derivatives. These are listed in table 26.

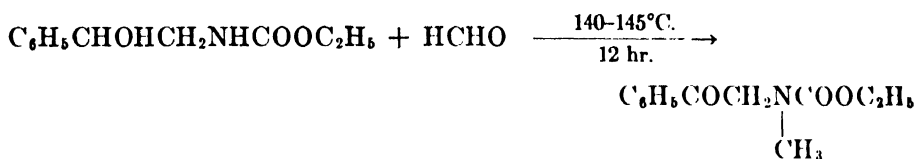N-Carbethoxyphenylethanolamine reacted with formaldehyde at 140–145°C. to give 55 per cent of ω-(N-methyl-N-carbethoxyamino)acetophenone (294).

$$C_6H_5CHOHCH_2NHCOOC_2H_5 + HCHO \xrightarrow[\text{12 hr.}]{140\text{–}145°C.}$$

$$C_6H_5COCH_2NCOOC_2H_5$$
$$|$$
$$CH_3$$

TABLE 26

N-Acyl-O-acylphenylethanolamines

PHENYLETHANOLAMINE	N-GROUP	O-GROUP	REFERENCES
p-Methoxy...	Benzoyl	Acetyl	(381, 475)
3,4-Dimethoxy...	Benzoyl	Benzoyl	(381)
3,4,5-Trimethoxy...	Benzoyl	Benzoyl	(381)
3,4-Methylenedioxy...	Benzoyl	Acetyl	(381)
	p-Nitrobenzoyl	p-Nitrobenzoyl	(485)
p-Benzoxy...	Benzoyl	Acetyl	(475)
	Benzoyl	Benzoyl	(758)

Treatment of N-homoveratroyl-3,4-dimethoxyphenylethanolamine for 5 min. with phosphorus pentoxide in boiling xylene gave a 30 per cent yield of papaverine (562).

$$\text{CH}_3\text{O}\overbrace{}\text{CHOHCH}_2\text{NHCOCH}_2\overbrace{}\text{OCH}_3 \xrightarrow{P_2O_5}$$
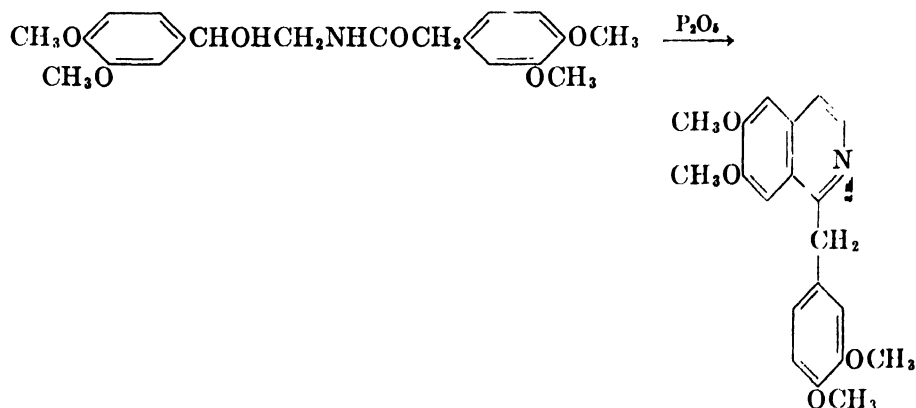
This type of ring closure to give compounds related to papaverine has been applied to a number of O-methyl ethers of N-acylated phenylethanolamines.

The ring closure has been effected with both phosphorus pentoxide in toluene and phosphorus oxychloride in xylene. These preparations are summarized in table 27.

Table 28 lists the N-acyl derivatives of O-methyl ethers of phenylethanolamines which have been prepared but not cyclized.

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TABLE 27

Papaverine derivatives

</div>

PHENYLETHANOLAMINE O-METHYL ETHER	N-ACYL GROUP	RING-CLOSING AGENT	REFERENCE
,4-Dimethoxy.	Benzoyl	P_2O_5	(628)
	Benzoyl	$POCl_3$	(476)
	Phenacetyl	$POCl_3$	(476)
	Homopiperonyl	$POCl_3$	(476)
	Homoveratroyl	$POCl_3$	(476)
	Homoveratroyl	P_2O_5	(628)
,4-Methylenedioxy.. . .	Benzoyl	$POCl_3$	(476)
	Phenacetyl	$POCl_3$	(476)
	Homopiperonyl	$POCl_3$	(476)
	Homoveratroyl	$POCl_3$	(476)
,5-Dimethoxy-3,4-methylenedioxy	Benzoyl	$POCl_3$	(471)
	Homopiperonyl	$POCl_3$	(471)
	Homoveratroyl	$POCl_3$	(471)

<div align="center">

TABLE 28

Acylated phenylethanolamine ethers

</div>
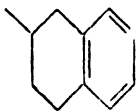
PHENYLETHANOLAMINE O-METHYL ETHER	N-ACYL GROUP	REFERENCE
2,4-Dimethoxy..	Phenacetyl	(471)
	Homopiperonyl	(471)
	Homoveratroyl	(471)
2,5-Dimethoxy-3,4-methylenedioxy .	Phenacetyl	(471)

Treatment of N-(o-carbomethoxybenzoyl)-3,4-methylenedioxyphenylethanol-amine-O-methyl ether with phosphorus oxychloride in boiling xylene gave the styrylimide (477).
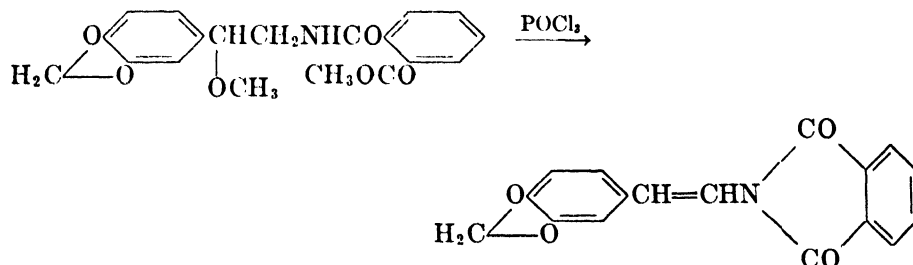
The same results were obtained by treating the N-(o-carboxybenzoyl) derivative of phenylethanolamine-O-methyl ether with phosphorus pentoxide. With phosphorus oxychloride the imide was obtained without the loss of methanol.

TABLE 29

Reductions of ω-(N-alkyl)aminoacetophenones

ω-(N-ALKYL)-AMINOACETOPHENONE	RING SUBSTITUENTS	REDUCING AGENT	YIELD	REFERENCE
			per cent	
		$H_2 + Ni$		(505)
		$H_2 + PtO_2$	90	(3)
		$H_2 + Pd$		(506)
	m-Hydroxy	$H_2 + Pd$		(443)
	p-Hydroxy	$H_2 + Pd$	90	(443)
	p-Hydroxy	$H_2 + Pd$	89	(146)
Methyl	p-Hydroxy	$H_2 + Pd$		(381)
	3,4-Dihydroxy	$H_2 + Pd$		(381)
	3,4-Dihydroxy	Al-Hg + aqueous H_2SO_4		(493)
	2-Hydroxy-3-methyl	$H_2 + Pt$		(28)
	3-Amino-4-hydroxy	$H_2 + PtO_2$		(657)
	3-Acetamino-4-hydroxy	$H_2 + PtO_2$		(657)
Ethyl	4-Hydroxy	$H_2 + Pd$	71	(146)
	3,4-Dihydroxy	Electrolysis		(493)
n-Propyl	p-Hydroxy	$H_2 + Pd$	68	(146)
Isopropyl	p-Hydroxy	$H_2 + Pd$	86	(146)
n-Butyl		$H_2 + PtO_2$	90	(3)
	p-Hydroxy	$H_2 + Pd$	83	(146)
Isobutyl	p-Hydroxy	$H_2 + Pd$	87	(146)
sec-Butyl	p-Hydroxy	$H_2 + Pd$	91	(146)
$tert$-Butyl	p-Hydroxy	$H_2 + Pd$	78	(146)
β-Phenethyl		$H_2 + Pd$		(20)
		$H_2 + Pd$	90	(20)

Besides the above amide chemistry p-hydroxyphenylethanolamine has been reported to give a blue color with sulfomolybdic acid (595). 3,4-Methylenedioxyphenylethanolamine gave a quaternary iodide when treated with methyl iodide (83).

Both N-n-butyl- and N-isobutyl-phenylethanolamines have been prepared by alkylating phenylethanolamine with n-butyl and isobutyl iodides, respectively (361). N-Methyl-3,4-methylenedioxyphenylethanolamine has been prepared by alkylating N-benzoyl-3,4-methylenedioxyphenylethanolamine with methyl io-

dide and then removing the benzoyl group by hydrolysis (83). Similar alkylation of piperonalphenylethanolamine followed by hydrolysis gave N-methylphenyl-ethanolamine.

In general the other preparations of N-alkylphenylethanolamines parallel those used for the unsubstituted compounds. Probably the most widely used is the reduction of the corresponding ω-(N-alkylamino)acetophenone. For convenience the numerous compounds prepared in this way are summarized in table 29.

In addition, 3-acetamino-4-hydroxy-ω-(N-methyl-N-acetylamino)acetophenone has been reduced to the corresponding phenylethanolamine by means of hydrogen and a platinum oxide catalyst (657).
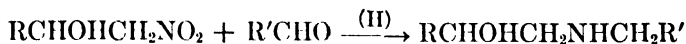
TABLE 30

Reductive debenzylations

SUBSTITUTED ω-(N-METHYL-N-BENZYL)-AMINOACETOPHENONE	REDUCING AGENT	YIELD	REFERENCE
		per cent	
	H_2 + Ni		(335)
p-Hydroxy	H_2 + Ni		(335)
2,5-Dimethoxy	H_2 + PtO_2		(48)
2-Methoxy-5-methyl	H_2 + Pt		(28)
3-Chloro-4-hydroxy	H_2 + Pt	95	(229)
3-Chloro-4-acetoxy	H_2 + Pt	97	(229)
3-Fluoro-4-hydroxy	H_2 + Pt	85	(229)
3-Chloro-4-hydroxy (N-ethyl)	H_2 + Pt	90	(229)

Certain ω-(N-methyl-N-benzylamino)acetophenones have been simultaneously reduced and debenzylated to give the corresponding N-methylphenylethanol-

$$RCOCH_2N\begin{matrix} CH_3 \\ \diagdown \\ CH_2C_6H_5 \end{matrix} \xrightarrow{(H)} RCHOHCH_2NHCH_3$$
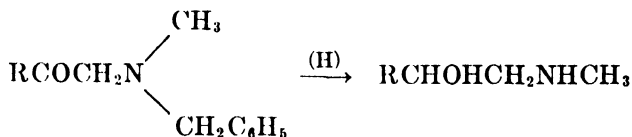
amines. These preparations are summarized in table 30.

A number of N-alkylphenylethanolamines have been prepared by the reductive alkylation of the corresponding β-nitro-α-phenethyl alcohol by means of an alde-

$$RCHOHCH_2NO_2 + R'CHO \xrightarrow{(H)} RCHOHCH_2NHCH_2R'$$

hyde and zinc and acetic acid as the reducing agent. These preparations are summarized in table 31.

Another very common method for preparing N-alkylphenylethanolamines is to treat a styrene halohydrin with the appropriate primary amine. These prepara-

$$RCHOHCH_2X + R'NH_2 \rightarrow RCHOHCH_2NHR'$$

tions are summarized in table 32.

When the methyl ether of styrene bromohydrin was treated with methylamine, a 33 per cent yield of the methyl ether of phenylethanolamine was obtained (465). This same reaction has been utilized successfully with the methyl ethers of 3,4-dimethoxystyrene bromohydrin and 3,4-methylenedioxystyrene bromohydrin.

TABLE 31

Reductive alkylations

β-NITRO-α-PHENETHYL ALCOHOL	ALDEHYDE	YIELD	REFERENCE
		per cent	
	Formaldehyde		(528)
3,4-Diacetoxy..........	Formaldehyde		(527)
	Formaldehyde		(360)
	n-Heptaldehyde	30	(360)
	Benzaldehyde	17	(360)
	Piperonal	32	(360)
	3,4-Diacetoxybenzaldehyde	51	(360)
	3-Methoxy-4-acetoxybenzaldehyde	22	(360)
	Furfural	28	(360)

TABLE 32

N-Alkylphenylethanolamines from styrene halohydrins

SUBSTITUTED STYRENE	HALOGEN IN HALOHYDRIN	AMINE	REFERENCE
	I	Aniline	(361)
3,4-Dimethoxy.......................	Br	Methylamine	(54)
3,4-Dimethoxy*.........	Br	Methylamine	(474)
3,4-Methylenedioxy...........................	Cl	Methylamine	(549)
3,4-Methylenedioxy...	Br	Methylamine	(54)
3,4-Methylenedioxy†..........................	Br	Methylamine	(474)
3,4-Dihydroxy.............................	Cl	Methylamine	(100, 472)
3,4-Dihydroxy.............................	Br	Methylamine	(100, 497)
Bromo-3,4-dihydroxy....................... ..	Br	Methylamine	(100)

* In this case the α-methylamino-β-phenethylalcohol also was isolated in the ratio of one to four of the β-methylamino-α-phenethylalcohol.
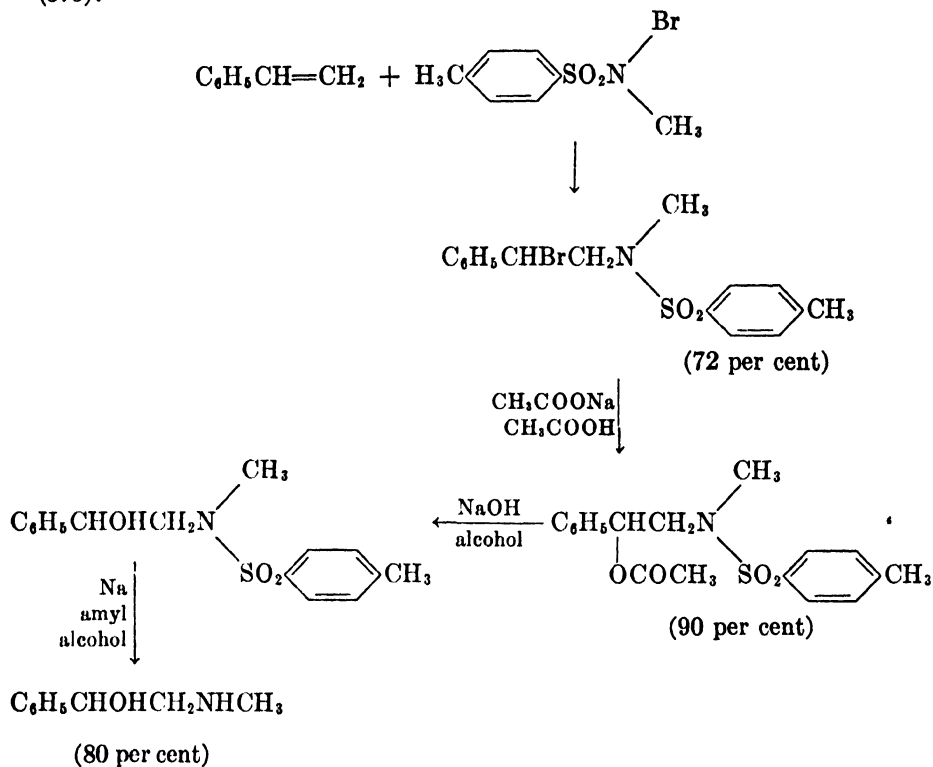
† Here the two isomers occurred in equal quantities.

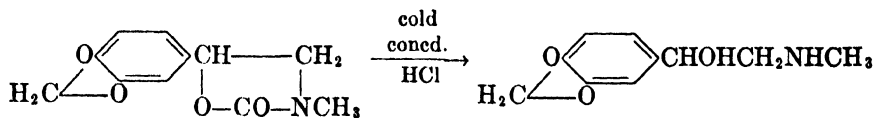A closely related method is the reaction of styrene oxide with a primary amine to give an N-alkylphenylethanolamine (189). Phenylethanolamines prepared successfully in this way include N-ethyl- (56 per cent yield), N-n-butyl- (64 per cent yield), N-n-dodecyl- (70 per cent yield), and N-β-hydroxyethyl- (63 per cent yield). In the case of the n-butyl compound some 2,6-diphenyl-4-n-butyl-morpholine was isolated as a by-product.
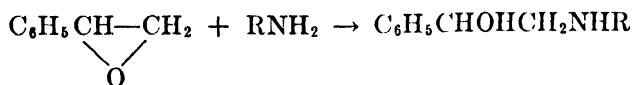
$$C_6H_5CH\underset{O}{\overset{}{\diagdown\diagup}}CH_2 + RNH_2 \rightarrow C_6H_5CHOHCH_2NHR$$

An interesting synthesis of N-methylphenylethanolamine is outlined below (375):

$$C_6H_5CH{=}CH_2 + H_3C\underset{}{\bigcirc}SO_2N\overset{Br}{\underset{CH_3}{\diagup}}$$

$$\downarrow$$

$$C_6H_5CHBrCH_2N\overset{CH_3}{\underset{SO_2\bigcirc CH_3}{\diagup}}$$

(72 per cent)

$$\underset{\substack{CH_3COONa \\ CH_3COOH}}{\Big\downarrow}$$

$$C_6H_5CHOHCH_2N\overset{CH_3}{\underset{SO_2\bigcirc CH_3}{\diagup}} \xleftarrow[\text{alcohol}]{NaOH} C_6H_5CHCH_2N\overset{CH_3}{\underset{\substack{| \\ OCOCH_3 \;\; SO_2\bigcirc CH_3}}{}}$$

Na
amyl
alcohol

(90 per cent)

$$\Big\downarrow$$

$$C_6H_5CHOHCH_2NHCH_3$$

(80 per cent)

When this method was applied to N-methyl-p-fluorophenylethanolamine, the overall yield from p-fluorostyrene was 56 per cent (229).

N-Methyl-3,4-methylenedioxyphenylethanolamine has been prepared by the hydrolysis reaction shown below (664).

$$H_2C\underset{O}{\overset{O}{\Big\langle}}\bigcirc\underset{\substack{| \\ O-CO-NCH_3}}{\overset{CH-\!-\!-CH_2}{}}\xrightarrow[\text{HCl}]{\substack{\text{cold} \\ \text{concd.}}} H_2C\underset{O}{\overset{O}{\Big\langle}}\bigcirc CHOHCH_2NHCH_3$$

N-Benzylphenylethanolamine has been prepared by the reduction of diphenyloxazole (219).

$$C_6H_5C\overset{O-CC_6H_5}{\underset{N-\!-CH}{\Big\|}}\xrightarrow{\substack{Na \\ \overline{C_2H_5OH}}} C_6H_5CHOHCH_2NHCH_2C_6H_5$$
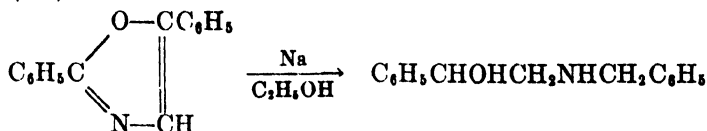
Recently a number of N-alkylphenylethanolamines have been prepared by the reductive amination of the corresponding phenylglyoxals (225a).

N-Methylphenylethanolamine has been alkylated with phenacyl bromide and with α-bromopropiophenone (770).

$$C_6H_5CHOHCH_2NHCH_3 \ + \ C_6H_5COCH_2Br \ \rightarrow$$

$$C_6H_5CHOHCH_2\underset{\underset{CH_3}{|}}{N}CH_2COC_6H_5$$
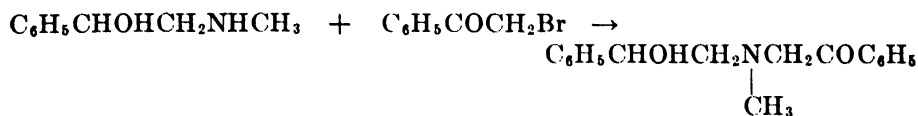
Other N,N-dialkylphenylethanolamines generally have been prepared by the same methods previously described for the less highly substituted compounds.
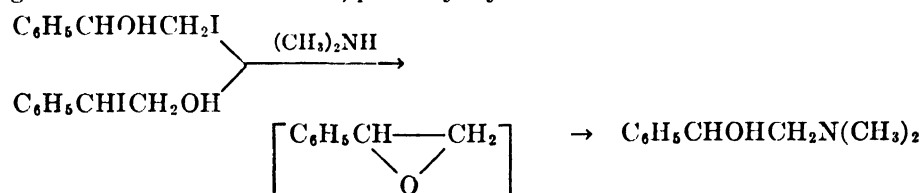
<div align="center">

TABLE 33

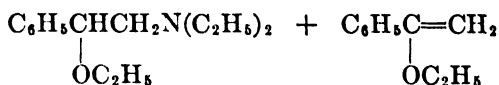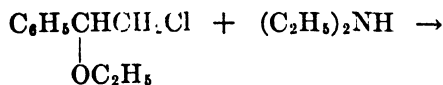*N,N-Dialkylphenylethanolamines from ω-aminoacetophenones*
</div>

NUCLEAR-SUBSTITUTED ω-AMINOACETOPHENONE	SUBSTITUENTS ON NITROGEN ATOM	REDUCING AGENT	YIELD	REFERENCE
			per cent	
	Dimethyl			(742)
	Diethyl	$H_2 + PtO_2$	73–75	(484)
	Di-n-butyl	$(i\text{-}C_3H_7O)_3Al$	69	(272)
	—CH₂CH₂ \ O / —CH₂CH₂	$H_2 + Pd$	87.5	(630)
	—CH₂ / \ —CH₂CH₂ (phenyl)	$H_2 + Pd$	91	(20)
p-Bromo............	Diethyl	$(i\text{-}C_3H_7O)_3Al$	70	(165)
	Di-n-propyl	$(i\text{-}C_3H_7O)_3Al$	70	(165)
	Di-n-butyl	$(i\text{-}C_3H_7O)_3Al$	93	(165)
	Pentamethylene	$(i\text{-}C_3H_7O)_3Al$	81	(165)
p-Hydroxy..........	Dimethyl	$H_2 + Pd$	75	(146)
3,4-Dihydroxy..	Dimethyl	Electrolysis		(493)
2,5-Dimethoxy.......	Dimethyl	$H_2 + PtO_2$		(48)

In table 33 are listed those N,N-dialkylphenylethanolamines which have been prepared by the reduction of the corresponding ω-(N,N-dialkylamino)acetophenone.

A number of N,N-dialkylphenylethanolamines have been prepared from the corresponding styrene halohydrin and a secondary amine. These preparations are summarized in table 34.

It is of interest that N,N-dimethylphenylethanolamine was obtained from β-iodo-β-phenethyl alcohol as well as from styrene iodohydrin (744). This suggests a common intermediate, probably styrene oxide.

$$\left. \begin{array}{l} C_6H_5CHOHCH_2I \\[2ex] C_6H_5CHICH_2OH \end{array} \right\rangle \xrightarrow{(CH_3)_2NH} \left[\begin{array}{c} C_6H_5CH\!-\!-\!CH_2 \\ \diagdown \; O \; \diagup \end{array} \right] \rightarrow C_6H_5CHOHCH_2N(CH_3)_2$$

The isomeric β-dimethylamino-β-phenethyl alcohol was synthesized by the following method and its derivatives were shown to have different properties from those of N,N-dimethylphenylethanolamine (744).

$$C_6H_5CH_2COCl \xrightarrow{Br_2} C_6H_5CHBrCOCl \xrightarrow{C_2H_5OH}$$

$$C_6H_5CHBrCOOC_2H_5 \xrightarrow{(CH_3)_2NH}$$

$$\underset{\underset{N(CH_3)_2}{|}}{C_6H_5CHCOOC_2H_5} \xrightarrow[C_2H_5OH]{Na} \underset{\underset{N(CH_3)_2}{|}}{C_6H_5CHCH_2OH}$$

Additional evidence for an oxide intermediate is found in the cases of 3,4-dimethoxy- and 3,4-methylenedioxy-styrene bromohydrins, where two different products are obtained on treatment with amines (474).

(4:1)

(1:1)

(CH₃)₂NH

(mostly)

The ethyl ether of styrene chlorohydrin reacted with diethylamine at 90–128°C. to give 69 per cent of O,N,N-triethylphenylethanolamine together with a little α-ethoxystyrene (315). The same reaction occurred with dimethylamine (744).

$$C_6H_5\underset{\underset{OC_2H_5}{|}}{CHCH_2Cl} + (C_2H_5)_2NH \rightarrow$$

$$C_6H_5\underset{\underset{OC_2H_5}{|}}{CHCH_2N(C_2H_5)_2} + C_6H_5\underset{\underset{OC_2H_5}{|}}{C=CH_2}$$

The methyl ethers of both 3,4-dimethoxy- and 3,4-methylenedioxy-styrene bromohydrins reacted with dimethylamine to give the corresponding N,N-dimethylphenylethanolamines, the former in quantitative yield (474).

TABLE 34

N,N-Dialkylphenylethanolamines from styrene halohydrins

SUBSTITUTED STYRENE HALOHYDRIN	SECONDARY AMINE	HALOGEN IN HALOHYDRIN	YIELD	REFERENCE
			per cent	
	Diethyl	Cl	66	(189)
	Diamyl	Cl	63	(189)
	Diethanol	Cl	63	(189)
	Dimethyl	I		(742, 744)
3,4-Methylenedioxy..................	Dimethyl	Br	90	(577)
	Dimethyl	Br		(474)

TABLE 35

N,N-Dialkylphenylethanolamines from styrene oxide

SECONDARY AMINE	YIELD	REFERENCE
	per cent	
Dimethyl....	Quantitative	(742, 743)
Di-n-propyl...........................	91	(189)
Di-n-butyl.......................	92	(189)
Diethanol.........	89	(189)
Morpholine...	80	(189)

Several N,N-dialkylphenylethanolamines have been prepared by treating styrene oxide with the appropriate secondary amine. These preparations are summarized in table 35.

Styrene oxide reacted with hydrazine, N,N-dimethylhydrazine, and N,N-diethylhydrazine in xylene solution at 120–140°C. to give the corresponding phenylethanolhydrazines in 29, 22, and 37 per cent yields, respectively (62). In the first case some completely alkylated hydrazine appeared as a by-product.

$$C_6H_5\underset{\underset{O}{\diagdown\diagup}}{CH-CH_2} + N_2H_4 \rightarrow C_6H_5CHOHCH_2NHNH_2 +$$

$$(C_6H_5CHOHCH_2)_2NN(CH_2CHOHC_6H_5)_2$$
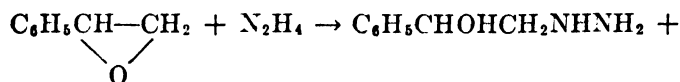
Quaternary salts in this series have been prepared by treating a styrene halo-hydrin with the appropriate tertiary amine. Styrene bromohydrin reacted with pyridine to give 59 per cent of the quaternary bromide (618).

$$C_6H_5CHOHCH_2Br + C_6H_5N \rightarrow C_6H_5CHOHCH_2NC_5H_5^+Br^-$$
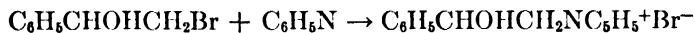
Styrene iodohydrin gave small amounts of quaternary iodides with trimethyl-amine and dimethylbenzylamine, together with larger amounts of acetophenone (80 per cent in the trimethylamine reaction) (745).

Quaternary pyridinium bromides also have been prepared by hydrogenating in the presence of a platinum oxide catalyst the corresponding derivatives of ω-aminoacetophenone (30 per cent yield) (618) and of 3-methoxy-4-acetoxy-ω-aminoacetophenone (20 per cent yield) (619). In the latter case some material in which the pyridine ring also was reduced likewise was isolated. 3-Methoxy-4-hydroxyphenacylpyridinium bromide was too insoluble for catalytic hydrogenation.

d-Phenylethanolamine has been alkylated with methyl iodide and sodium methoxide to give 80 per cent of the quaternary iodide (597). N,N-Dimethyl-phenylethanolamine yielded quaternary salts with both methyl iodide and methyl chloride (744). A quaternary iodide was obtained by treating N,N-dimethyl-2,5-dimethoxyphenylethanolamine with methyl iodide (48). Treatment with silver chloride gave the corresponding quaternary chloride. The methyl and ethyl ethers of N,N-dimethylphenylethanolamine (744) and the methyl ether of N,N-dimethyl-3,4-methylenedioxyphenylethanolamine (474) added methyl iodide to give quaternary iodides. The same compound was prepared by treating N,N-dimethyl-3,4-methylenedioxyphenylethanolamine with sodium and then with methyl iodide.
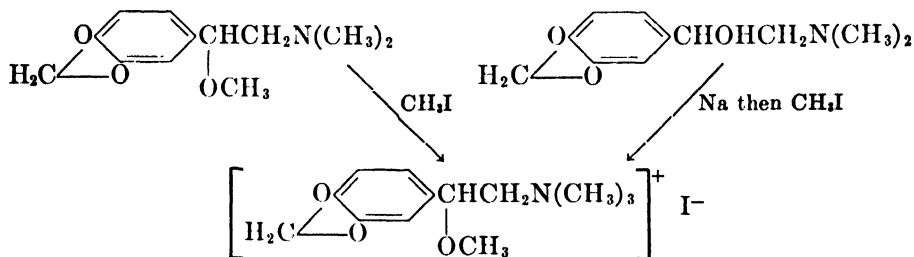
N-Methylphenylethanolamine gave an orange-yellow color when warmed with 4 per cent hydrogen peroxide containing sodium chloride (675). The hydro-chloride of N-methyl-p-hydroxyphenylethanolamine gave a blue color with sul-fomolybdic acid (595).

Treatment of N-β-phenethylphenylethanolamine with benzoyl chloride gave 88 per cent of the O-benzoate (20). With N-β-tetrahydronaphthylphenylethanol-amine the yield was 67 per cent.

N-Methyl-m-hydroxyphenylethanolamine hydrochloride reacted with acetyl chloride in glacial acetic acid to give 80 per cent of N-methyl-O,m-diacetoxy-

phenylethanolamine hydrochloride (119). The analogous dipropionyl derivative was prepared by the same method in 83 per cent yield.

$$
\underset{HO}{\diagdown}\!\!\!\bigcirc\!\!\!\diagup CHOHCH_2NHCH_3 \cdot HCl \quad \xrightarrow[\text{CH}_3\text{COOH}]{\text{CH}_3\text{COCl}} \quad CH_3COO\!\!-\!\!\bigcirc\!\!-\!\!\underset{OCOCH_3}{\overset{HCl}{CHCH_2\overset{\cdot}{N}HCH_3}}
$$

<center>(80 per cent)</center>
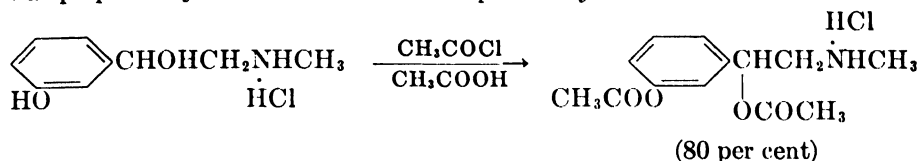
Some of the acetylation reactions of *N*-methyl-3,4-dihydroxyphenylethanol-amine (adrenaline) are summarized in equation form below (118):
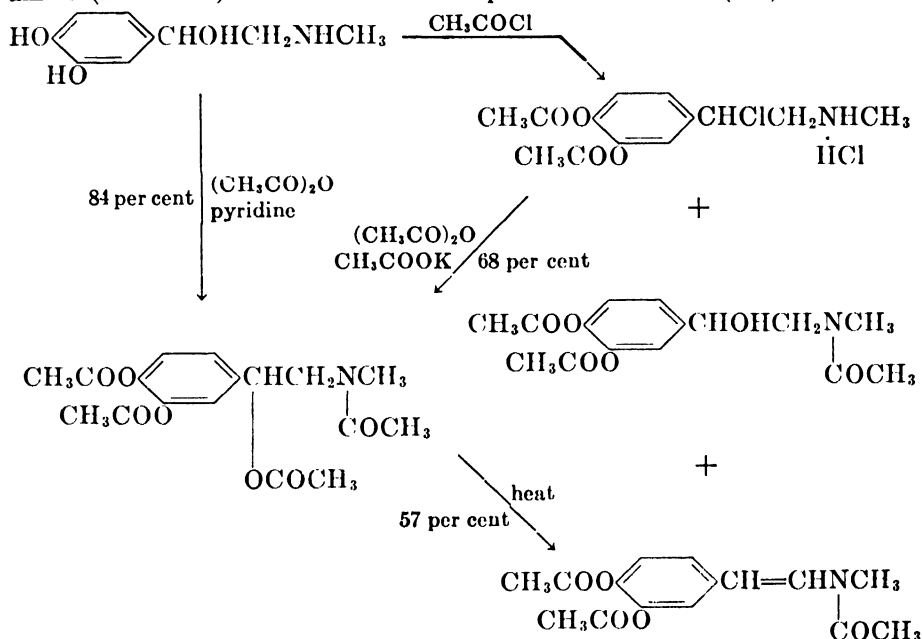
N-Methyl-3,4-methylenedioxyphenylethanolamine formed a picrate and reacted with phenyl isothiocyanate to give a thiourea (549). The latter compound lost water to give a substituted tetrahydrothiazole.
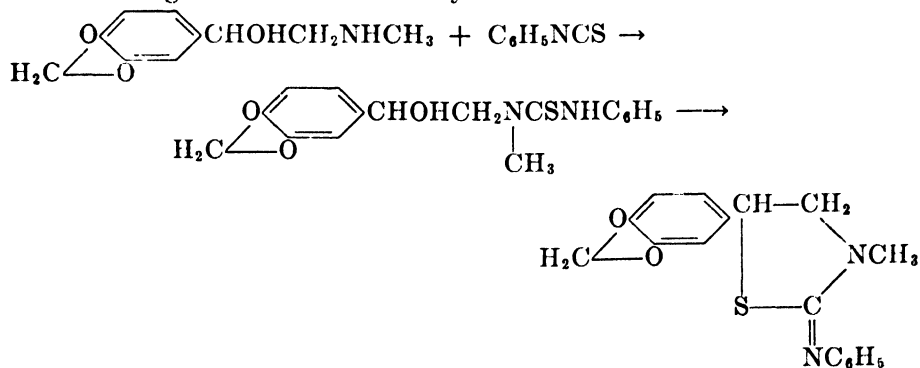
N-Benzylphenylethanolamine reacted with nitrous acid to give an N-nitroso derivative and with hydriodic acid to give benzyl β-phenethylamine (219).

A number of sulfonamides of N-alkyl-β-bromo-β-phenethylamines have been prepared by adding N-alkyl-N-bromosulfonamides to styrene (375). These

$$C_6H_5CH{=}CH_2 \ + \ RSO_2N\diagup\overset{R'}{\underset{Br}{\diagdown}} \ \rightarrow \ C_6H_5CHBrCH_2N\diagup\overset{R'}{\underset{SO_2R}{\diagdown}}$$
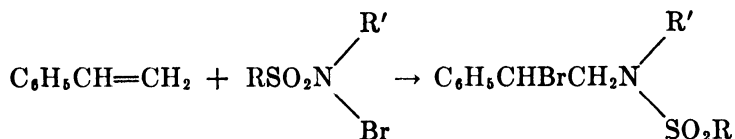
preparations are summarized in table 36.

The N-methyl-N-p-toluenesulfonyl compound was dehydrobrominated by means of both quinoline and alcoholic sodium ethoxide. Treatment with sodium in amyl alcohol gave methyl-β-phenethylamine. The N-benzyl-N-p-toluenesulfonyl compound also was dehydrobrominated with alcoholic sodium ethoxide.

TABLE 36

Styrene and N-bromosulfonamides

N-ALKYL GROUP	SULFONAMIDE	YIELD
		per cent
Methyl...........................	p-Toluene	72
Benzyl...........................	p-Toluene	
Benzyl..	Benzene	
β-Bromo-α-phenethyl.................	p-Toluene	
β-Phenethyl............	p-Toluene	

The numerous esters of the N,N-dialkylphenylethanolamines are summarized in table 37, together with their methods of preparation.

The benzoate of N,N-dimethyl-3,4-methylenedioxyphenylethanolamine also was prepared in 78 per cent yield by the acid chloride method (577). The above-mentioned N,N-dimethyl-O-acetylphenylethanolamine added methyl iodide to give a quaternary salt (746).

No discussion of the reactions of phenylethanolamines would be complete without mentioning the elucidation of the structure of adrenaline. In 1903 Abel (1), who prepared and saponified the monobenzoyl derivative, suggested the empirical formula $C_{10}H_{13}NO_3$. Pauly (546) showed the correct formula to be $C_9H_{13}NO_3$, recalled the previous evidence for a catechol nucleus, and postulated the five possible side chains. On the basis of a tribenzenesulfonyl derivative with benzenesulfonyl chloride, a tribenzoyl derivative with benzoic anhydride, an addition product with methyl iodide, and oxalic acid from treatment with hydrogen peroxide or potassium permanganate, v. Furth (250) suggested the structural formula $CH_3NC_2HOHC_6H_6(OH)_2$. In 1904 Pauly (547) prepared a dibenzoyl derivative, using benzoyl chloride and sodium bicarbonate so as not to touch

the phenolic hydroxyl groups. From this reaction and the fact that methylamine was obtained on degradation, the presence of a methylamino group was indicated. Pauly favored the formula:

$$HO-\langle\bigcirc\rangle-CHCH_2OH$$
$$HO \qquad NHCH_3$$
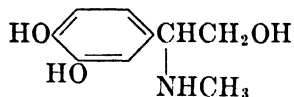
TABLE 37
N,N-Dialkylphenylethanolamine esters

SUBSTITUENTS ON NITROGEN ATOM	ESTER	METHOD OF PREPARATION	YIELD	REFERENCE
			per cent	
Dimethyl..................	Acetate	Anhydride		(746)
	Acetate	Acid chloride	96	(119)
	Benzoate	Acid chloride		(742, 744)
Diethyl....................	p-Nitrobenzoate	Acid chloride	89–91	(481)
	p-Aminobenzoate	Reduction of nitro	77–81	(484)
	2-Ethylhexoate	Acid	53	(189)
Di-n-propyl.................	Butyrate	Acid	72	(189)
Di-n-butyl.......	Acetate	Anhydride	63	(189)
	3,5-Dinitrobenzoate	Acid chloride		(272)
Diamyl.....................	Butyrate	Acid	54	(189)
Diethanol..................	Triacetate	Anhydride	75	(189, 196)
—CH₂CH₂ ⟍ O ⟋ —CH₂CH₂	Propionate	Acid	77	(189)
	Benzoate	Acid chloride	60–65	(630)
	Cinnamate	Acid chloride	88	(630)
—CH₂CH₂⟨⟩ —CH₃	Benzoate	Acid chloride	88	(20)

In the same year Jowett (357) favored the correct structure for adrenaline, although Pauly had suggested it as a possibility:

$$HO-\langle\bigcirc\rangle-CHOHCH_2NHCH_3$$
$$HO$$
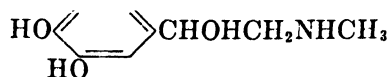
Jowett's evidence was that oxidation with potassium permanganate gave methyl-

amine, formic acid, and oxalic acid; the fusion product with potassium hydroxide gave the color reactions of catechol; and methylation with methyl iodide followed by oxidation with potassium permanganate gave veratric acid and trimethylamine. Aldrich (11) summarized the known chemistry of adrenaline and also favored the correct structure. In 1906 Friedman (245) obtained a tribenzenesulfonyl derivative by treating adrenaline with benzenesulfonyl chloride and sodium hydroxide. Oxidation with chromic acid in acetic acid yielded a ketone, tribenzenesulfonyl adrenalone, which Friedman synthesized. This reaction differentiated between the two structures suggested by Pauly and showed the one favored by Jowett and Aldrich to be correct.

Treatment of adrenaline with catechol oxidase yielded a red indole quinone (275). A similar compound containing iodine was obtained with potassium iodate in acetic acid (64, 617). Some of its chemistry is shown below (64):
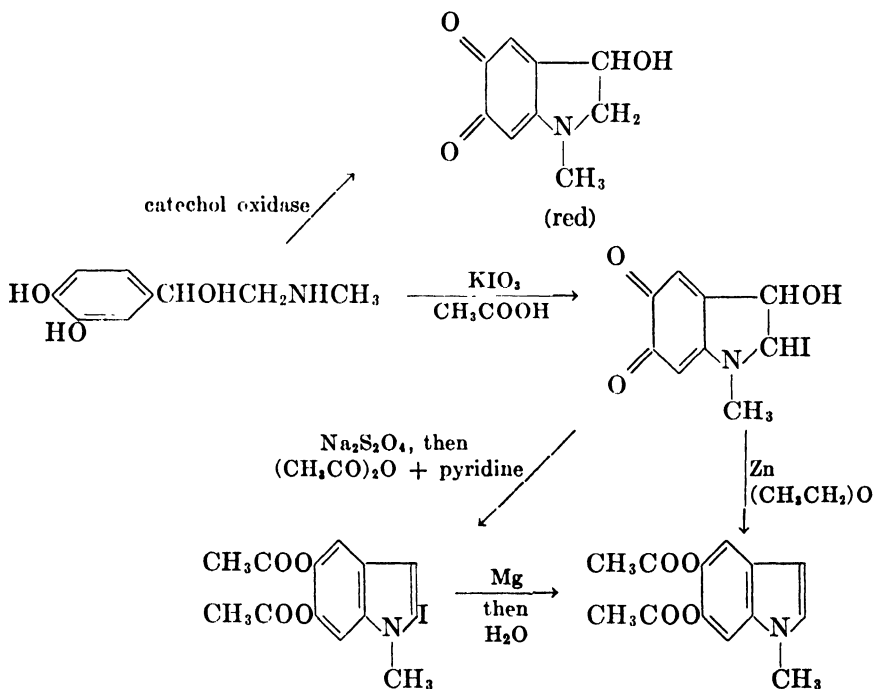
Treatment of adrenaline with lead dioxide in aqueous acetic acid gave a compound which has been postulated as an isomer of that obtained with catechol oxidase (593). In this case the ring closure was postulated as taking place ortho rather than para to the 3-hydroxyl group.

β-Amino-β-phenethyl alcohol usually has been prepared by the reduction of ω-hydroxyacetophenone oxime by means of sodium amalgam (414, 611, 727) in 44 per cent yield (251). α-Phenethylamine has appeared as a by-product (414) to the extent of 27 per cent (251).

$$C_6H_5CCH_2OH \xrightarrow{\text{Na-Hg}} C_6H_5CHCH_2OH + C_6H_5CHCH_3$$
$$\underset{NOH}{\|} \qquad\qquad \underset{NH_2}{|} \qquad\qquad \underset{NH_2}{|}$$
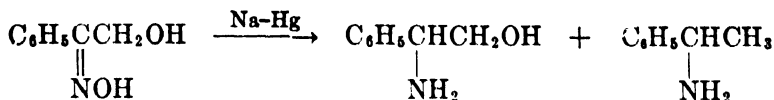
An alternative route is the reduction of ethyl phenylglycinate by means of sodium and ethanol (27 per cent yield) (442) or hydrogen and Raney nickel in methanol solution at 40°C. for 9 hr. (59 per cent yield) (540). With longer times the benzene ring was saturated and at higher temperatures the amino group was methylated. At 100°C. no reduction occurred in the presence of copper chromite. β-Amino-β-phenethyl alcohol has been prepared by treating 2-amino-4-phenyloxazoline with alcoholic potassium hydroxide (727).

$$C_6H_5CH-N$$
$$| \qquad\quad \diagdown$$
$$\qquad\qquad CNH_2 \xrightarrow{\text{KOH}} C_6H_5CHCH_2OH + K_2CO_3 + NH_3$$
$$| \qquad\quad \diagup \qquad\qquad\qquad \underset{NH_2}{|}$$
$$H_2C-O$$
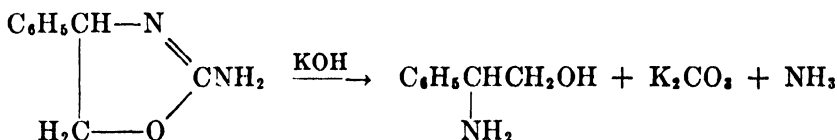
Treatment with benzoyl chloride gave the N-benzoyl derivative (414, 442, 611). This compound has been acylated further with acetic anhydride and sodium acetate (414) or pyridine (611) to give the N-benzoyl-O-acetyl derivative and with benzoyl chloride and pyridine to give the dibenzoyl derivative (611, 727) and the tribenzoyl derivative (611). Treatment of β-amino-β-phenethyl alcohol with acetic anhydride in pyridine gave the diacetyl derivative (611). The N-dichloroacetate and the urea also have been prepared (414), and β-amino-β-phenethyl alcohol has been resolved as the tartrate (611). Oxidation with dilute acid potassium permanganate gave phenylglycine (611). Distillation gave diphenylpyrazine (611).

$$C_6H_5CHCH_2OH \xrightarrow[\text{H}_2\text{SO}_4]{\text{KMnO}_4} C_6H_5CHCOOH$$
$$\underset{NH_2}{|} \qquad\qquad\qquad \underset{NH}{|}$$
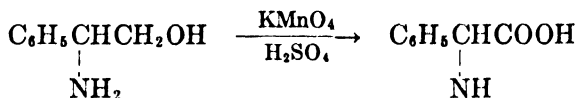
β-Amino-β-phenethyl alcohol reacted with a mixture of phosphorus trichloride and phosphorus pentachloride to give β-chloro-α-phenethylamine (611) in 76 per cent yield (442) and 56 per cent yield (251). Neither hydrochloric acid

$$C_6H_5CHCH_2OH \xrightarrow[\text{PCl}_5]{\text{PCl}_3} C_6H_5CHCH_2Cl$$
$$\underset{NH_2}{|} \qquad\qquad\qquad \underset{NH_2}{|}$$
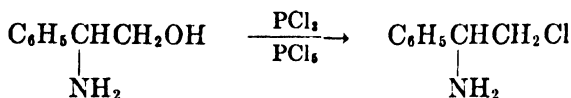
at 100°C. nor thionyl chloride was effective (251). β-Chloro-α-phenethylamine has also been prepared by treating the nitrogen trichloride adduct of styrene with hydrogen chloride (142, 143). β-Chloro-α-phenethylamine has been benzoylated (142) and acetylated by standard means and also resolved as the tartrate

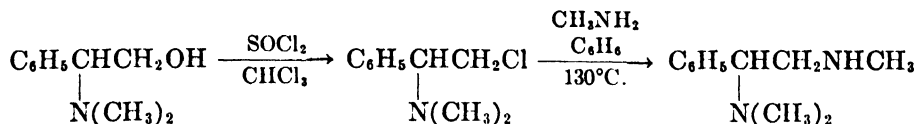(611). Certain other reactions are shown below (251):

C_6H_5CH—CH_2 (as picrate) C_6H_5CH—N
　　　　　＼／   　＼
　　　　　　NH   　CSH
　　　　　　↑ NaOH   CS$_2$ ↗ H_2C— —S
　　　　　　│ H$_2$O
　　　　　　│ 60–70°C.

$C_6H_5CHCH_2Cl$ $C_6H_5CHCH_2OCOC_6H_5$
　　│   │
　　NH$_2$ NH$_2$·HCl

　│   ＼ C_6H_5COCl H_2O ↗   │ NaOH
　│ $C_6H_5CHCH_2Cl$ ／ boil $C_6H_5CHCH_2OH$
HSCN│   │   │
　│   NHCOC$_6$H$_5$ NHCOC$_6$H$_5$
　│   ＼ KOH   ↑ H$_2$O
　↓   C$_2$H$_5$OH ＼   │ 100°C.

C_6H_5CH—S C_6H_5CH—N
　│   ＼   │   ＼
　│   C=NH   │   CC$_6$H$_5$
　H$_2$C—NH／   H$_2$C——O／
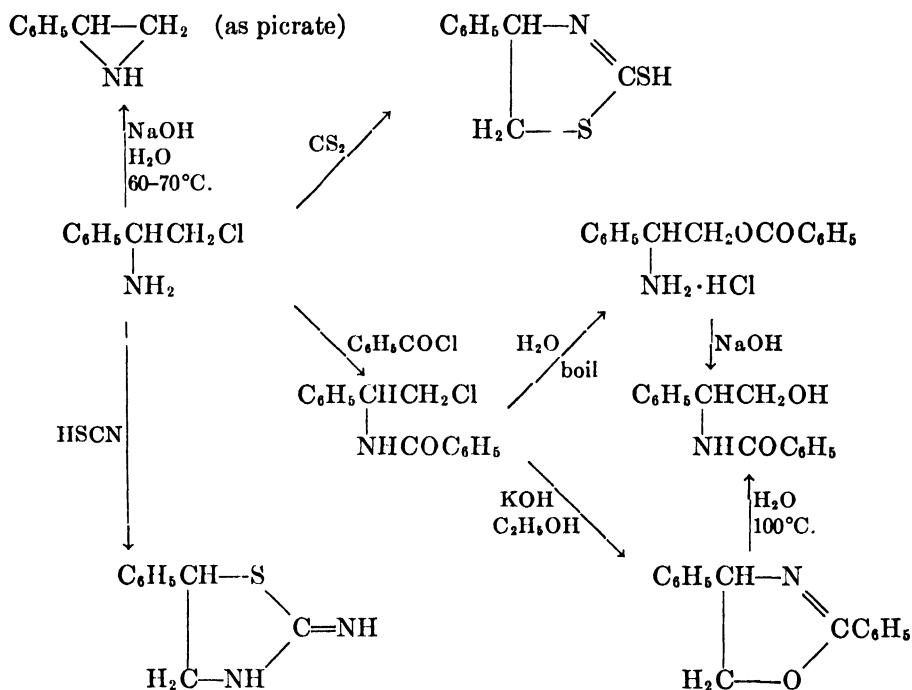
The N-p-nitrobenzoyl derivative has been prepared by the Schotten–Baumann reaction in 92 per cent yield and cyclized to the oxazoline in 86 per cent yield by heating with alcoholic potassium hydroxide at 70–75°C. for 1 min. (442).

β-Amino-β-phenethyl alcohol reacted with a mixture of phosphorus tribromide and phosphorus pentabromide to give β-bromo-α-phenethylamine (611). Fuming hydrobromic acid at 100°C. was ineffective (251). The last-named compound was resolved as the malate and the active N-acetyl compound prepared by treating this salt with acetic anhydride (611). The malate also was reduced to α-phenethylamine by means of hydrogen in the presence of a palladium catalyst.

The preparation of β-N-methylamino-β-3,4-dimethoxyphenethyl alcohol, β-N-methylamino-β-3,4-methylenedioxyphenethyl alcohol and β-N,N-dimethylamino-β-3,4-methylenedioxyphenethyl alcohol along with the isomeric phenylethanolamines from the corresponding styrene bromohydrins has been mentioned previously (474). The β-N,N-dimethylamino-β-3,4-methylenedioxyphenethyl alcohol added methyl iodide to form a quaternary salt. β-N,N-Dimethylamino-β-phenethyl alcohol has been prepared in 32 per cent yield by reducing ethyl N,N-dimethylphenylglycinate with sodium in alcohol (744). It has been characterized as the hydrochloride, picrate, gold chloride, o-benzoyl hydrochloride, morpholone, methiodide, and methyl chloride. Treatment with thionyl chloride in chloroform replaced the hydroxyl group with chlorine and further treatment

with methylamine in benzene at 130°C. gave a 60 per cent overall yield of the substituted phenylethylenediamine (63).

$$C_6H_5CHCH_2OH \xrightarrow[\text{CHCl}_3]{\text{SOCl}_2} C_6H_5CHCH_2Cl \xrightarrow[\text{130°C.}]{\overset{\text{CH}_3\text{NH}_2}{\text{C}_6\text{H}_6}} C_6H_5CHCH_2NHCH_3$$

$$\underset{\text{N(CH}_3)_2}{|} \qquad\qquad \underset{\text{N(CH}_3)_2}{|} \qquad\qquad \underset{\text{N(CH}_3)_2}{|}$$

Treatment of β-iodo-β-phenethyl alcohol with trimethylamine in benzene gave mostly phenylacetaldehyde and its polymers, together with some of the expected quaternary iodide (745). With dimethylbenzylamine the expected quaternary iodide also was obtained, along with a trace of acetophenone in this case.

Since the completion of this manuscript a long paper has appeared describing the preparation of a large number of N,N-dialkylphenylethanolamines (463).

E. β-Alkoxy- and β-acyloxystyrenes

The commonest preparation of β-alkoxystyrenes is the addition of alcohols to phenylacetylene in the presence of a basic catalyst at around 135°C. Potassium hydroxide (33, 448) has served for the methoxy- and ethoxy-styrenes (77 per cent

$$C_6H_5C{\equiv}CH + ROH \rightarrow C_6H_5CH{=}CHOR$$
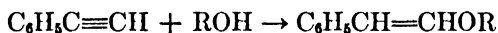
yield) (531) and the sodium alkoxide (519) for the methoxy- (68 per cent yield) (521), ethoxy- (531) (69 per cent yield) (521), n-propoxy- (69 per cent yield) (521), and isobutoxy-styrenes (75 per cent yield) (521). ω-Chlorophenylacetylene also added ethanol in the presence of potassium hydroxide or sodium ethoxide (531).

Closely related to this method is the reaction of a β-chloro- or β-bromo-styrene with a sodium alkoxide or alcoholic alkali, with phenylacetylene as a possible intermediate. Treatment of β-chlorostyrene with potassium hydroxide (207, 227) or sodium ethoxide (207) at 180°C. gave β-ethoxystyrene in 67 per cent yield (197). β-Bromostyrene reacted with sodium methoxide to give 12 per cent of β-methoxystyrene, 28 per cent of phenylacetylene, and a 55 per cent recovery of the β-bromostyrene (456). Similarly β-bromostyrene reacted with potassium hydroxide in ethanol (448) to give 60 per cent of phenylacetylene and 17 per cent of β-ethoxystyrene (531), although a later report states the yield of β-ethoxystyrene to be almost quantitative (292).

Over porous plate at 200°C. phenylacetaldehyde dimethylacetal gave 36 per

$$C_6H_5CH_2CH(OCH_3)_2 \xrightarrow{\text{200°C.}} C_6H_5CH{=}CHOCH_3$$
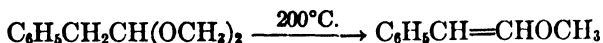
cent of β-methoxystyrene (672). At 250°C. the di-n-propylacetal gave 70 per cent of β-n-propoxystyrene.

Treatment of phenylmagnesium bromide with ethoxyacetal gave a mixture of β-ethoxystyrene and styrene glycol diethyl ether (292, 695, 697). The analogous mixture was obtained from o-tolyl-, m-tolyl-, and 2,4-dimethylphenyl-magnesium iodides and p-tolyl- and p-chlorophenyl-magnesium bromides (697).

Pyrolysis (145°C.) of β,β-diethoxy-α-phenylpropionic acid gave β-ethoxysty-

$$(C_2H_5O)_2CHCHCOOH \xrightarrow{145°C.} C_6H_5CH=CHOC_2H_5 + CO_2 + C_2H_5OH$$
$$\overset{|}{C_6H_5}$$
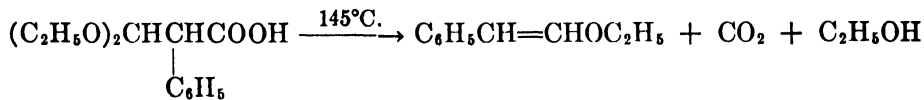
rene (780). The same compound was obtained by heating benzal-ω-ethoxy-acetophenone with potassium hydroxide (172).

$$C_6H_5COC=CHC_6H_5 + KOH \xrightarrow{heat} C_6H_5CH=CHOC_2H_5 + C_6H_5COOK$$
$$\overset{|}{OC_2H_5}$$
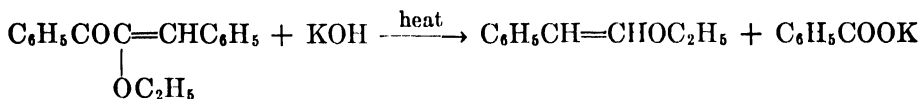
Pyrolysis (260°C.) of α-phenoxycinnamic acid gave 13–14 per cent of phenyl phenylacetate and the remainder of the product was β-phenoxystyrene (710). A yield of 63–64 per cent has been reported (711).

$$C_6H_5CH=CCOOH \xrightarrow{260°C.} C_6H_5CH=CHOC_6H_5 + C_6H_5CH_2COOC_6H_5$$
$$\overset{|}{OC_6H_5}$$
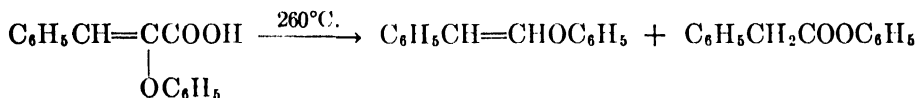
At 260–270°C. α-p-tolyloxycinnamic acid underwent the same reaction.

β-Phenoxystyrene reacted with ethyl alcohol in the presence of potassium hydroxide at 200°C. to give β-ethoxystyrene and a little styrene (710). β-Methoxy-styrene has been postulated as an intermediate in the preparation of phenyl-acetaldehyde by treating styrene iodohydrin methyl ether with silver nitrate (741).

Phenylacetaldehyde was produced when β-methoxystyrene (672), β-ethoxy-styrene (419, 521, 531, 710), β-n-propoxystyrene (672), β-isobutoxystyrene (519), and β-phenoxystyrene (710) were boiled with dilute sulfuric acid. β-Ethoxy-styrene yielded phenylacetaldehyde merely on steam distillation (207, 227). A 74 per cent yield of phenylacetaldehyde was obtained by passing the vapors of β-ethoxystyrene together with steam over a silica catalyst held at 215–225°C. (191, 197).

$$C_6H_5CH=CHOC_2H_5 \xrightarrow[215-225°C.]{H_2O, SiO_2} C_6H_5CH_2CHO$$
$$\text{(74 per cent)}$$
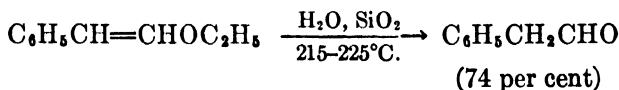
Phenylacetaldehyde also was obtained by passing, together with steam, β-ethoxy-styrene and phenylacetaldehyde acetal at 180–210°C. over silica impregnated with sodium bisulfate, and β-methoxystyrene and phenylacetaldehyde dimethyl-acetal at 210–235°C. over pumice impregnated with phosphoric acid (191). Phenylacetaldehyde (292, 695, 697) and the following analogs were obtained by boiling a mixture of the corresponding β-ethoxystyrene and styrene glycol diethyl ether with dilute sulfuric acid: o-methyl-, m-methyl-, p-methyl-, 2,4-dimethyl-, and p-chloro- (697).

β-Phenoxystyrene was unaffected by boiling alcoholic potassium hydroxide (710).

β-Acetoxystyrene has been prepared by treating phenylacetaldehyde with acetic anhydride in the presence of pyridine (95, 96) or sodium acetate (36, 226) in 80 per cent yield (292, 665). While the above method gave the *trans* isomer,

$$C_6H_5CH_2CHO + (CH_3CO)_2O \rightarrow C_6H_5CH=CHOCOCH_3 + CH_3COOH$$
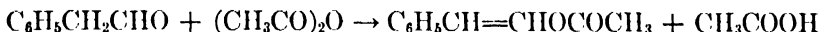
the *cis* isomer was produced by treating benzalacetone with peracetic or perbenzoic acid (95, 96).

Hydrogenation of β-acetoxystyrene in the presence of a palladium catalyst gave 82.5 per cent of β-phenethyl acetate (678). Oxidation with ozone gave benzaldehyde and benzoic acid (665) and with peracetic acid gave benzoic and formic acids (96). Hydrolysis with water at 100–110°C. (both isomers) (95) gave phenylacetaldehyde and acetic acid (665).

F. α-Alkoxy- and α-acyloxystyrenes

One of the commonest preparations of α-alkoxystyrenes has been to distil or pyrolyze the corresponding ketal of acetophenone. This method has been ap-

$$\begin{matrix} C_6H_5CCH_3 \\ \| \\ (OR)_2 \end{matrix} \longrightarrow \begin{matrix} C_6H_5C=CH_2 \\ | \\ OR \end{matrix} + ROH$$
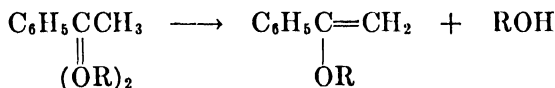
plied successfully to obtain the following styrenes: α-methoxy- (140) (86 per cent yield, 672), α-ethoxy- (140, 141) (85 per cent yield, 334), and α-n-propoxy- (140) (97 per cent yield, 672). Treatment of acetophenone ketal with acetyl chloride and pyridine gave α-ethoxystyrene, while acetyl chloride alone gave 1,3,5-triphenylbenzene (141).

Decarboxylation of a β-alkoxycinnamic acid gives an α-alkoxystyrene.

$$\begin{matrix} C_6H_5C=CHCOOH \\ | \\ OR \end{matrix} \xrightarrow{\text{heat}} \begin{matrix} C_6H_5C=CH_2 \\ | \\ OR \end{matrix} + CO_2$$
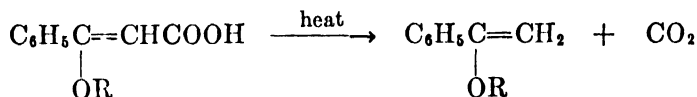
The styrenes listed in table 38 have been prepared in this way. Closely related to this method is the pyrolysis of a β-phenyl-β,β-dialkoxypropionic acid. This has been used for the preparation of α-methoxy- (33, 518, 520) and α-ethoxystyrenes (33). The by-products are the acetophenone ketal (518, 520) and the β-alkoxycinnamic acid (520).

$$\begin{matrix} C_6H_5CCH_2COOH \\ \| \\ (OCH_3)_2 \end{matrix} \xrightarrow{100°C.} \begin{matrix} C_6H_5C=CH_2 \\ | \\ OCH_3 \end{matrix} +$$

$$\begin{matrix} C_6H_5CCH_3 \\ \| \\ (OCH_3)_2 \end{matrix} + \begin{matrix} C_6H_5C=CHCOOH \\ | \\ OCH_3 \end{matrix}$$
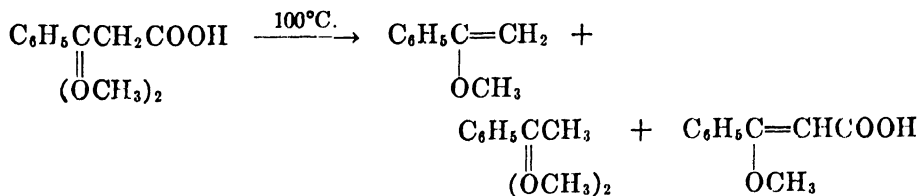
The third general method for preparing α-alkoxystyrenes is to dehydrohalogenate the appropriate ether of a styrene halohydrin. Treatment of styrene chlorohydrin ethyl ether with sodium hydroxide in methanol gave α-ethoxystyrene (314) in 70 per cent yield (302). The same result was effected in the case of p-methoxystyrene chlorohydrin ethyl ether by means of alcoholic sodium ethoxide (583).

A convenient synthesis is that shown below for α-ethoxystyrene (433).

$$C_6H_5MgBr \quad + \quad CH_2BrCHBr(OC_2H_5) \quad \longrightarrow$$

$$C_6H_5CHCH_2Br \quad \xrightarrow[\text{solid KOH}]{\text{distil from}} \quad C_6H_5C{=}CH_2$$
$$\underset{\text{(66 per cent)}}{OC_2H_5} \qquad\qquad \underset{\text{(62 per cent)}}{OC_2H_5}$$
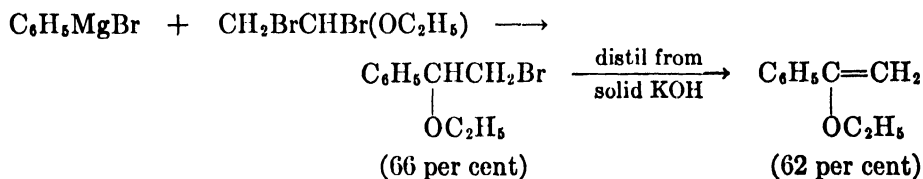
TABLE 38

α-Alkoxystyrenes from β-alkoxycinnamic acids

STYRENE PREPARED	YIELD	REFERENCES
α-Methoxy.................................		(518, 519, 520)
α-Ethoxy................................		(139, 448, 519)
α-Phenoxy...............................	Nearly quantitative	(635)
α-(o-Tolyloxy)		(635)
α-(m-Tolyloxy)		(636)
α-(p-Tolyloxy)		(635)
α-(2,4-Dimethylphenoxy)................		(638)
α-(2-Isopropyl-5-methylphenoxy).........		(633)
α-(p-Methoxyphenoxy)..............		(637)
α-(α-Naphthoxy).........................		(635)

The method has been applied successfully for the preparation of the following styrenes (434): α-methoxy- (65 per cent, –), α-n-propoxy- (66 per cent, –), α-n-butoxy- (57 per cent, 70 per cent), α-isoamoxy (81 per cent, –), and p-chloro-α-methoxy- (51 per cent, 59 per cent). The yields in parentheses are for the two successive steps in the synthesis. Styrene bromohydrin methyl ether has been dehydrohalogenated with sodium methoxide in methanol to give 45 per cent of α-methoxystyrene (796).

α-Methoxy-, α-ethoxy-, and α-amoxy-styrenes have been prepared by treating the corresponding ether of styrene iodohydrin with alcoholic potassium hydroxide (741).

α-Ethoxystyrene was a by-product in the reaction between styrene chlorohydrin ethyl ether and ammonia or diethylamine (315). When 2-methyl-4-methoxy-5-isopropylstyrene dichloride was treated with alcoholic sodium ethoxide, the three products shown below were obtained (583).

$$(CH_3)_2CH$$

$$CH_3O\langle\_\rangle CHClCH_2Cl \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3O\langle\_\rangle CCl{=}CH_2 +$$

$$CH_3 \hspace{6cm} CH_3$$

$$(CH_3)_2CH \quad OC_2H_5 \hspace{2cm} (CH_3)_2CH \quad OC_2H_5$$

$$CH_3O\langle\_\rangle \overset{|}{C}HCH_2Cl + CH_3O\langle\_\rangle \overset{|}{C}{=}CH_2$$

$$CH_3 \hspace{6cm} CH_3$$
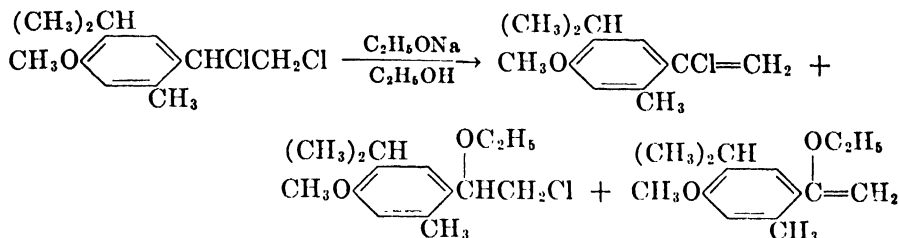
α-Alkoxystyrenes react readily with dilute acids to give acetophenone. This has been shown to be true with the following styrenes: α-methoxy- (518, 519,
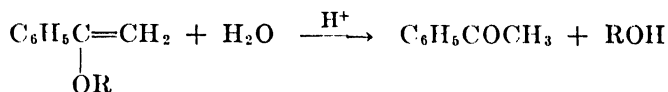
$$C_6H_5\underset{\overset{|}{O}R}{C}{=}CH_2 + H_2O \xrightarrow{H^+} C_6H_5COCH_3 + ROH$$

796), α-ethoxy- (302, 314, 519), α-phenoxy- (635), α-(o-tolyloxy)- (635), α-(m-tolyloxy)- (636), α-(p-tolyloxy)- (635), and α-(α-naphthoxy)- (635). Houben and Führer reported that α-ethoxystyrene also could be hydrolyzed to acetophenone by means of alcoholic alkali (312, 314). Hoering maintained that this was not true (301), and the controversy went on for some time (302, 313). No one since has reported the alkaline hydrolysis of an α-alkoxystyrene.

α-Ethoxystyrene has been reported to react instantly with bromine, nitrous acid, and phenyldiazonium acetate in acetic acid (508).

Claisen (140) showed that when α-methoxystyrene was heated, propiophenone was produced. Similarly α-ethoxystyrene gave butyrophenone and α-n-propoxystyrene gave valerophenone. This reaction has been studied in detail and at 300°C. the following yields were obtained: propiophenone, 65 per cent; butyrophenone, 58 per cent; valerophenone, 30 per cent; caprophenone, 74 per cent; p-chloropropiophenone, 68 per cent; isoenanthylophenone, not given (434). In the pyrolysis of α-methoxystyrene to give propiophenone some methane also was isolated as well as 11 per cent of 1,2-dibenzoylpropane. From α-ethoxystyrene there was obtained, besides butyrophenone, 7 per cent of 1,2-dibenzoylbutane and ethane containing 6 per cent of ethylene. Propane containing 16

$$C_6H_5\underset{\overset{|}{O}C_2H_5}{C}{=}CH_2 \xrightarrow[\text{1 hr.}]{300°C.} C_6H_5CO(CH_2)_2CH_3 +$$

$$C_6H_5CO\underset{\overset{|}{C_2H_5}}{C}HCH_2COC_6H_5 + C_2H_6 + CH_2{=}CH_2$$
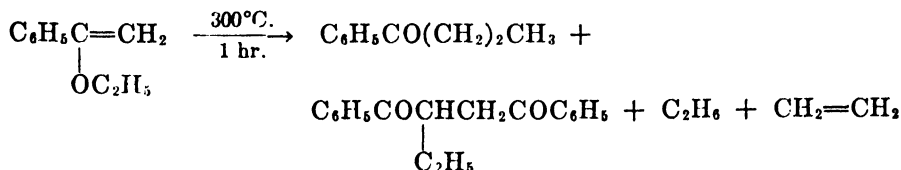
per cent of propylene was isolated from the α-n-propoxystyrene pyrolysis and 4 per cent of 1,2-di(p-chlorobenzoyl)propane was the by-product in the p-chloro-α-methoxystyrene pyrolysis. Besides the isoenanthylophenone obtained in the α-isoamoxystyrene pyrolysis, 2-methylbutane, acetophenone, and dibenzoylethane were produced. The copyrolysis of α-n-butoxystyrene and p-

chloro-α-methoxystyrene gave acetophenone and propiophenone besides a variety of other products. .

These reactions have been considered from a theoretical angle (434) and have been shown to proceed in two stages, both of which kinetic studies have shown to be of the second order (464).

$$C_6H_5\underset{\underset{OCH_3}{|}}{C}=CH_2 \xrightarrow{\text{heat}} C_6H_5COCH_2CH_3$$

$$C_6H_5\underset{\underset{OCH_3}{|}}{C}=CH_2 + C_6H_5COCH_2CH_3 \xrightarrow{\text{heat}}$$

$$CH_4 + C_6H_5COCH\underset{\underset{CH_3}{|}}{CH_2}COC_6H_5$$
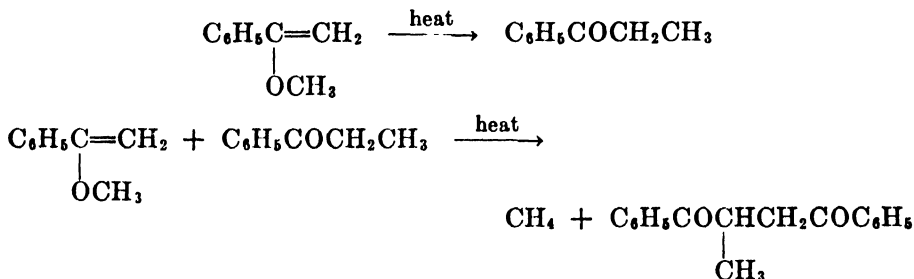
A bimolecular mechanism has been suggested for the first of the above reactions (517).

$$\begin{array}{c} OCH_3 \dashrightarrow CH_2=CC_6H_5 \\ | \qquad\qquad\qquad | \\ C_6H_5C=CH_2 \longleftarrow\dashleftarrow CH_3O \end{array} \rightarrow 2C_6H_5COCH_2CH_3$$
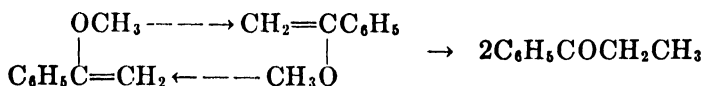
α-Methoxystyrene also reacts with halogen-containing compounds by a similar mechanism.

$$\begin{array}{c} OCH_3 \dashrightarrow X \\ | \qquad\qquad | \\ C_6H_5C=CH_2 \qquad R \end{array} \rightarrow C_6H_5COCH_2R + CH_3X$$
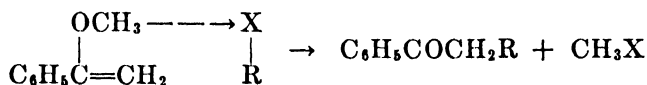
Examples are shown by the equations on page 291. In all cases a large excess of the halogen compound was employed.

Just as α-alkoxystyrenes react with aralkyl ketones as shown in the previous section, so do they react with other compounds containing activated hydrogen atoms (701). In the equations on page 292 are shown a number of such reactions for α-methoxystyrene. A large excess of the second reactant always was employed.

The preparation of α-styrylthioethers by decarboxylating the appropriate cinnamic acid has been utilized in the case of the phenyl (637), o-tolyl (634), and 2,4-dimethylphenyl (634) derivatives. Both the phenyl (637) and o-tolyl (634) compounds were converted to acetophenone and the corresponding mercaptan by treatment with dilute aqueous acids.

$$C_6H_5\underset{\underset{SC_6H_5}{|}}{C}=CHCOOH \xrightarrow{\text{heat}} C_6H_5\underset{\underset{SC_6H_5}{|}}{C}=CH_2 \xrightarrow{\text{H}^+} C_6H_5COCH_3 + C_6H_5SH$$
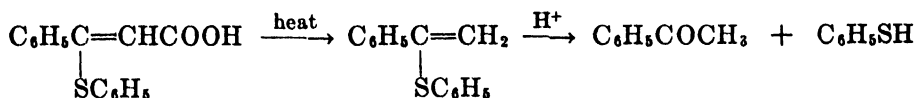
α-Acetoxystyrene has been prepared in 34 per cent yield by treating styrene bromohydrin acetate with quinoline in the presence of hydroquinone (479) and in 19 per cent conversion by treating acetophenone with ketene in the presence of

$C_6H_5CH_2Br$
220°C.
→ $C_6H_5CO(CH_2)_2C_6H_5$ + CH_3Br + $C_6H_5COCH_2CH_3$
(51 per cent)   (a little)

$CH_3(CH_2)_3Br$
245°C.
→ $C_6H_5CO(CH_2)_4CH_3$
(28 per cent)

$ClCH_2COOC_2H_5$
200°C.
→ $C_6H_5CO(CH_2)_2COOC_2H_5$ + $C_6H_5COCH_3$ + C_6H_5
(36 per cent)   (25 per cent)

C_6H_5COCl
(small amount)
180°C.
→ C_6H_5CO — COC_6H_5

C_6H_5COCl
(excess)
180°C.
→ C_6H_5 — C_6H_5

$C_6H_5C=CH_2$
|
OCH_3

$$C_6H_5C{=}CH_2$$
$$\underset{OCH_3}{|}$$

$\xrightarrow[250°C.]{C_6H_5CH_3}$ $C_6H_5CO(CH_2)_2C_6H_5 + CH_4$
(35 per cent)

$\xrightarrow[200-300°C.]{p\text{-}CH_3OC_6H_4CH_3}$ $C_6H_5CO(CH_2)_2{-}\!\!\bigcirc\!\!{-}OCH_3$
(26 per cent)

$\xrightarrow[250°C.]{1,3,5\text{-}C_6H_3(CH_3)_3}$ $C_6H_5CO(CH_2)_2{-}\!\!\bigcirc\!\!\overset{CH_3}{\underset{CH_3}{}}$
(21 per cent)

$\xrightarrow[250°C.]{C_6H_5C_2H_5}$ $C_6H_5COCH_2\overset{CH_3}{\underset{|}{C}}HC_6H_5$
(24 per cent)

$\xrightarrow{C_6H_{12}}$ $C_6H_5COCH_2CH\big\langle\!\!\overset{CH_2CH_2}{\underset{CH_2CH_2}{}}\!\!CH_2$
(43 per cent)

$\xrightarrow[250°C.]{(C_6H_5)_2CH_2}$ $C_6H_5COCH_2CH(C_6H_5)_2 + C_6H_5COCH_3$
(27 per cent)   (17 per cent)

$+ \ C_6H_5COCH_2CH_2CH_3 + (C_6H_5)_2CHCH(C_6H_5)_2$
(20 per cent)

sulfuric acid (157a, 278). Acetophenone reacted with isopropenyl acetate in the presence of sulfuric acid to give 52 per cent of α-acetoxystyrene (577a).

$$C_6H_5COCH_3 + CH_3C\!\!=\!\!CH_2 \xrightarrow{\ H_2SO_4\ } C_6H_5C\!\!=\!\!CH_2 + CH_3COCH_3$$
$$\qquad\qquad\quad \underset{OCOCH_3}{|} \qquad\qquad\qquad\quad \underset{OCOCH_3}{|}$$
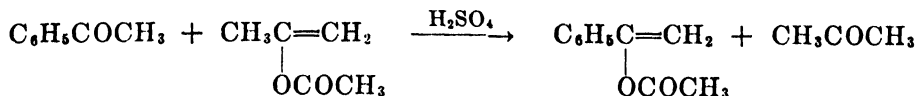
The compound added bromine to form a dibromide (278). With ethyl methyl ketone in the presence of sulfuric acid α-acetoxystyrene yielded 67 per cent of acetoxybutene (577b). Treatment of 2-hydroxy-5-carboxy-ω,ω-dichloroaceto-phenone with acetic anhydride and sodium acetate gave α,2-diacetoxy-5-carboxy-β,β-dichlorostyrene (138).
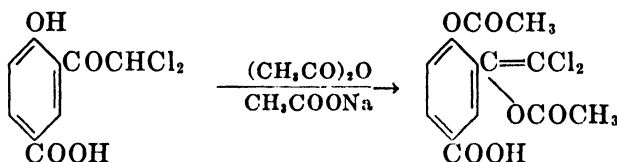
VII. ADDITION OF HYDROGEN HALIDES

In 1865 Erlenmeyer (202) reported that treatment of styrene with hydrochloric acid at 170°C. gave distyrene. Two years later Berthelot (75, 76, 77) listed the addition of hydrogen chloride as one of the characteristic reactions of styrene. Schramm (663) first formulated the product as α-chloroethylbenzene. This reaction has been patented (325, 328, 331, 339). Most of the examples employ

$$C_6H_5CH\!\!=\!\!CH_2 + HCl \rightarrow C_6H_5CHClCH_3$$

hydrogen chloride gas under pressure with xylene as a solvent, and yields up to 99 per cent (325, 328, 339) have been claimed.

The addition of hydrogen bromide to styrene was first reported by Bernthsen and Bender (71), who formulated the reaction as giving principally β-bromoethylbenzene and a little α-bromoethylbenzene. Subsequent investigators (31, 256a, 373, 565, 663) formulated the product correctly as α-bromoethylbenzene. The heat of this addition has been measured (460), and yields of 74 per cent (629) and 84 per cent (733, 768) have been reported.

At 125°C. in ethylbenzene as a solvent the product consisted of 63 per cent α-bromoethylbenzene and 30 per cent β-bromoethylbenzene (688). At 95°C. in the presence of benzoyl peroxide the product contained 92 per cent β-bromoethylbenzene and 7 per cent of the α-isomer. In chlorobenzene the ratio was 79 per cent β and 21 per cent α. With lauroyl peroxide and no solvent 80 per cent of product was obtained, of which 93 per cent was the α-isomer (768). When the mixture was diluted with pentane 75 per cent of product was isolated, of which 80 per cent was the β-isomer. With no peroxide present the addition gave primarily the α-isomer in the absence of a solvent or in carbon tetrachloride solution (724). Somewhat more β-isomer was obtained in benzene solution and still more in ligroin. Nickelous bromide accelerated the formation of the α-isomer and disturbed the effect of oxygen.

Styrene has been reported to add thiocyanic acid (372). No reaction occurred with hydrogen cyanide alone (401); in the presence of aluminum chloride and hydrogen chloride the product was polystyrene (776).

p-Divinylbenzene added hydrogen bromide in acetic acid solution to give *p*-bis(α-bromoethyl)benzene (342).

o-(β-Dimethylaminoethyl)styrene added both hydrogen chloride and hydrogen bromide (116). *o*-α-Bromoethylbenzyl bromide was obtained by treating *o*-bromomethylstyrene with fuming hydrobromic acid (110). In ether solution 3,4-methylenedioxystyrene added hydrogen bromide in normal fashion (466).

$$\text{H}_2\text{C} \underset{\text{C}}{\overset{\text{O}}{\diagdown}} \underset{}{\underset{}{\diagup}} \text{CH=CH}_2 + \text{HBr} \xrightarrow{\text{ether}} \text{H}_2\text{C} \underset{\text{O}}{\overset{\text{O}}{\diagdown}} \underset{}{\diagup} \text{CHBrCH}_3$$
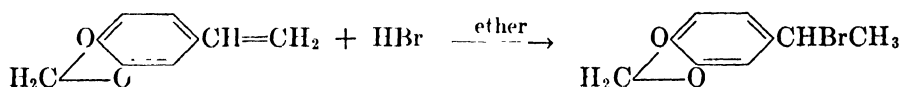
In benzene-pentane solution in the presence of benzoyl peroxide a low yield of the β-adduct was obtained from 3-methoxy-4-acetoxystyrene (619).

$$\text{CH}_3\text{COO} \underset{\text{CH}_3\text{O}}{\diagup} \underset{}{\diagdown} \text{CH=CH}_2 + \text{HBr} \xrightarrow{(\text{C}_6\text{H}_5\text{COO})_2}$$

$$\text{CH}_3\text{COO} \underset{\text{CH}_3\text{O}}{\diagup} \underset{}{\diagdown} \text{CH}_2\text{CH}_2\text{Br}$$
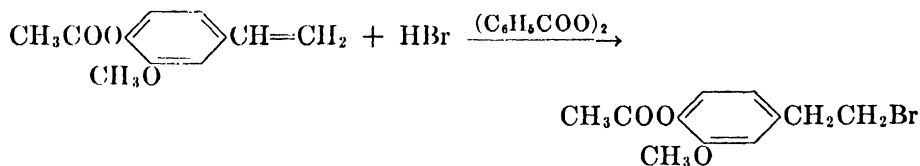
Normal addition of hydrogen bromide with the bromine atom going into the α-position also has been observed with 3,5-dibromo-4-hydroxystyrene (814), β,3,5-tribromo-4-hydroxystyrene (814), and 2,3,4-tribromo-4-hydroxystyrene (816). The quinoid forms of *p*-hydroxystyrenes add hydrogen bromide with the bromine going into the α-position (816).

α-Bromostyrene added hydrogen bromide very rapidly to give α,α-dibromoethylbenzene (725). With β-bromostyrene the addition was very slow. In the presence of nickelous bromide the product was styrene dibromide and in the presence of peroxide β,β-dibromoethylbenzene.

$$\text{C}_6\text{H}_5\text{CH=CHBr} + \text{HBr} \underset{\text{peroxide}}{\overset{\text{NiBr}_2}{\diagup \diagdown}} \begin{array}{c} \text{C}_6\text{H}_5\text{CHBrCH}_2\text{Br} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{CHBr}_2 \end{array}$$
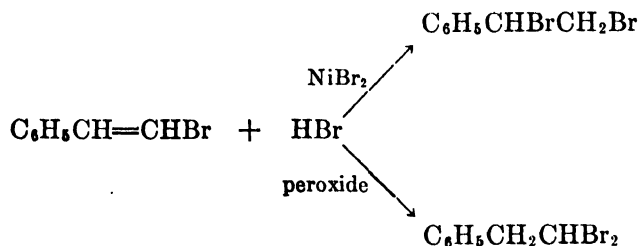
β-Phthalimidostyrene added hydrogen bromide in the normal fashion (628).

$$\text{C}_6\text{H}_5\text{CH=CHN} \underset{\text{CO}}{\overset{\text{CO}}{\diagup \diagdown}} \underset{}{\diagg} \xrightarrow{\text{HBr}} \text{C}_6\text{H}_5\text{CHBrCH}_2\text{N} \underset{\text{CO}}{\overset{\text{CO}}{\diagup \diagdown}} \underset{}{\diagg}$$

β-Nitrostyrene did not react with hydrogen bromide (571), and α-methoxy-

styrene gave 1,3,5-triphenylbenzene on treatment with hydrogen chloride (517). When treated with hydriodic acid, β-phenoxystyrene yielded phenol and β-phenylnaphthalene, with styrene diiodide as the postulated intermediate in the formation of the latter compound (711).

VIII. ADDITION OF WATER AND ALCOHOLS

The hydration of styrene has been mentioned in a patent but no experimental details were given (126). When styrene and deuterium oxide were heated for 100 hr. at 110°C., some exchange was noted (124). The exchange was catalyzed by both sodium hydroxide and sulfuric acid.

The sulfuric acid-catalyzed addition of alcohols to styrene at 135-150°C. has been reported in the case of methanol (90 per cent yield), ethanol (59 per cent yield), and 1-butanol (80 per cent yield) (704) to give the corresponding α-alkoxyethylbenzenes. With 2-propanol 50 per cent of the styrene reacted and the

$$C_6H_5CH{=}CH_2 + CH_3OH \xrightarrow[135-150°C.]{H^+} C_6H_5CHCH_3$$
$$\underset{OCH_3}{|}$$
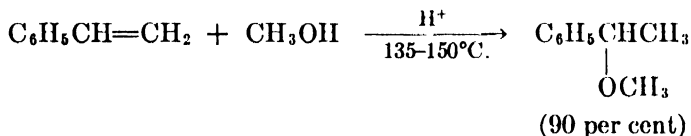
$$(90 \text{ per cent})$$

product was 23 per cent polymer and 77 per cent isopropyl ether. Some methanol addition has been observed in the titration of styrene with bromine and calcium bromide in methanol solution (490).

Styrene added saligenin (57 per cent yield) and 3,5-dimethyl-2-hydroxybenzyl alcohol (74 per cent yield) to give cyclic products (318).
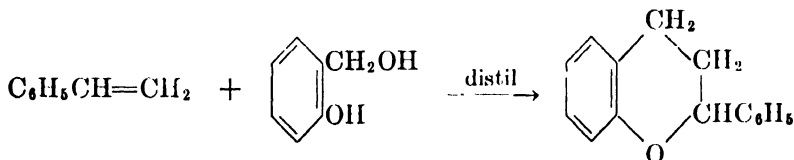
Methanol has been added to the quinoid forms of the following substituted styrenes: β 2,3,5-tetrabromo-4-hydroxy-, $\beta,\beta,2,3,5$-pentabromo-4-hydroxy-, and $\beta,\beta,2,3,5,6$-hexabromo-4-hydroxy- (816).
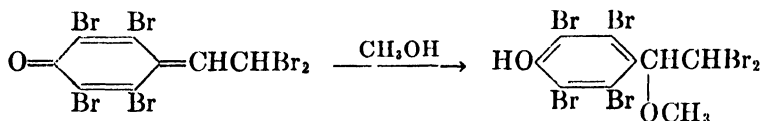
Meisenheimer and Heim (491) were the first to add methanol and ethanol to β-nitrostyrene. In the case of methanol their yield was 62 per cent. The reactions were conducted in the cold with the sodium alkoxide as the catalyst. When the reactants were allowed to stand 40 hr. at room temperature, bimolecular products were obtained in 15–35 per cent and 20 per cent yields, respectively (491, 492).

$$C_6H_5CH{=}CHNO_2 + CH_3OH \xrightarrow[\text{then } CO_2]{\underset{CH_3ONa}{}}$$

cold →

$$\underset{\underset{\textstyle OCH_3}{|}}{C_6H_5CHCH_2NO_2}$$

room temperature →

$$\underset{\textstyle CH_3O}{C_6H_5CH}{-}CHNO_2$$

$$C_6H_5CHCH_2NO_2$$

(15–35 per cent)
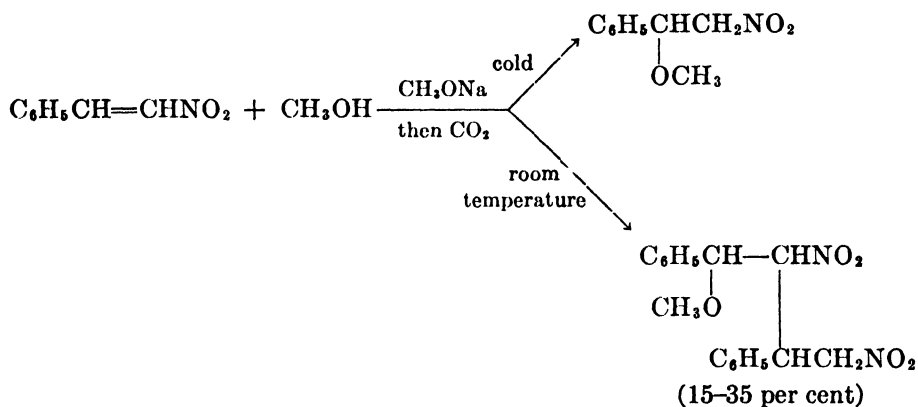
TABLE 39
β-Nitrostyrenes and alcohols

SUBSTITUTED β-NITROSTYRENE	ALCOHOL	CATALYST	YIELD	REFERENCE
			per cent	
	C_2H_5OH	None	0	(225)
	CH_3OH	CH_3ONa		(476)
β-Bromo	C_2H_5OH	None	14	(225)
o-Nitro-β-bromo	C_2H_5OH	None		(224)
m-Nitro	CH_3OH	NaOH		(441)
	C_2H_5OH	NaOH		(441)
p-Nitro	CH_3OH	KOH		(441)
	C_2H_5OH	KOH		(244)
p-Nitro-β-bromo	C_2H_5OH	None	100	(225)
	C_2H_5OH	None		(224)
o-Methoxy-β-bromo	CH_3OH	KOH		(608)
p-Methoxy-β-bromo	CH_3OH	KOH		(608)
2,4-Dimethoxy	CH_3OH	KOH		(471)
3,4-Dimethoxy	CH_3OH	CH_3ONa	67–72	(628)
	CH_3OH	CH_3ONa		(622)
	CH_3OH	CH_3ONa		(487)
	CH_3OH	CH_3ONa		(476)
3,4-Methylenedioxy	CH_3OH	CH_3ONa		(476)
	CH_3OH	CH_3ONa		(628)
3,4-Methylenedioxy-β-bromo	CH_3OH	KOH		(530)
2,5-Dimethoxy-3,4-methylenedioxy	CH_3OH	KOH		(471)

A little before the work of Meisenheimer and Heim, Thiele and Haeckel (737) had added methanol to β-bromo-β-nitrostyrene (97 per cent yield) and to β-bromo-β,p-dinitrostyrene in the presence of potassium hydroxide as a catalyst.

$$C_6H_5CH{=}CBrNO_2 + CH_3OH \xrightarrow[\text{then } H^+]{KOH} C_6H_5CHCHBrNO_2$$

$$\underset{\text{OCH}_3}{|}$$

(97 per cent)
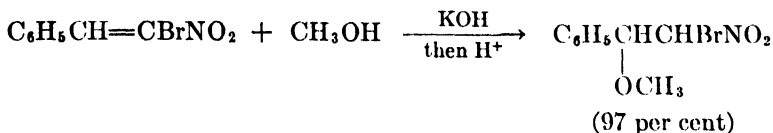
Since this early work a great many investigators have added alcohols to β-nitrostyrenes in the presence of alkaline catalysts. These reactions are summarized in table 39.

There have been a few examples of simultaneous bromination and alcohol addition as in the case of β,m-dinitrostyrene (243).
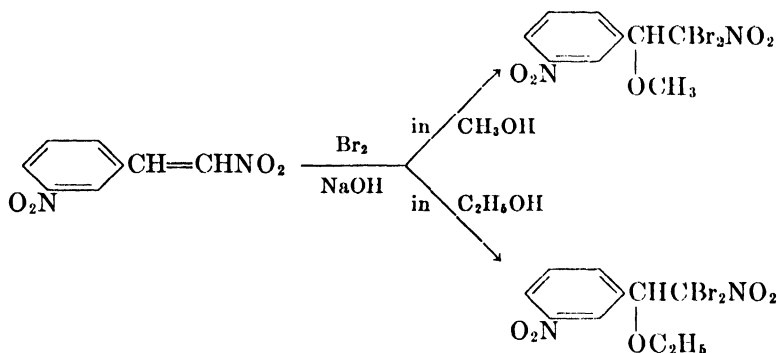
The same reaction has been carried out with β,p-dinitrostyrene in ethanol solution (224). An interesting alternate synthesis of β,m-dinitro-β,β-dibromo-α-methoxyethylbenzene, which also was applied to the α-ethoxy compound, is shown below (441).

(not isolated)
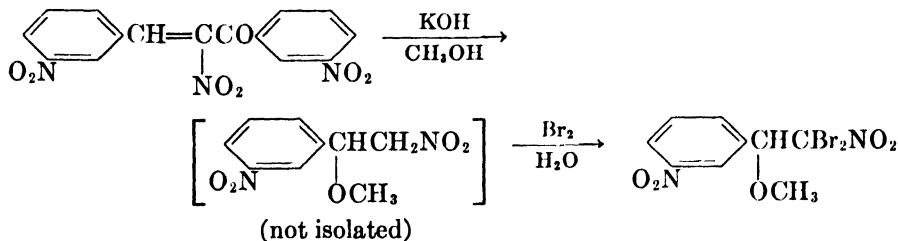
IX. ADDITION OF HYDROGEN SULFIDE, MERCAPTANS, SULFUR, THIOCYANOGEN, ETC.

Originally it was reported that no reaction occurred between styrene and liquid hydrogen sulfide (386). More recently it has been shown that bimolecular products are formed when styrene or p-methoxystyrene and hydrogen sulfide are heated in ethanol or 1-butanol solution in the presence of ammonia or the sodium alkoxide (340). Yields run as high as 80 per cent.

$$2C_6H_5CH{=}CH_2 + H_2S \xrightarrow[\text{NH}_3]{C_2H_5OH} C_6H_5CH{-}S{-}CHC_6H_5$$

$$\underset{CH_3}{|} \quad \underset{CH_3}{|}$$
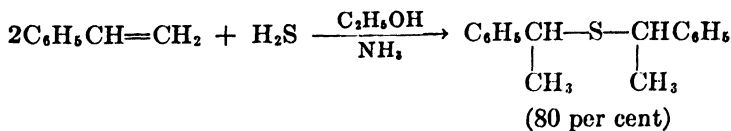
(80 per cent)

At 600°C. in the presence of a ferrous sulfide–alumina catalyst styrene reacted with hydrogen sulfide to give 60 per cent of benzothiophene (515).

$$C_6H_5CH=CH_2 + H_2S \xrightarrow[\text{FeS/Al}_2O_3]{600°C.} \text{[benzothiophene]} + 2H_2$$
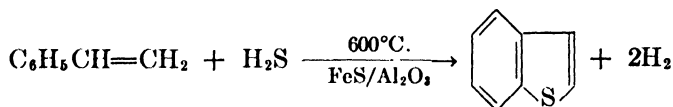
When treated with H_2S_2, styrene yielded metastyrene and a compound having the formula $C_8H_8S_2$ (304). With H_2S_3 the products were mono- and di-sulfides of styrene (386).

$$C_6H_5CH=CH_2 + H_2S_3 \longrightarrow \underset{\underset{S\text{——}S}{|\qquad|}}{C_6H_5CH\text{——}CH_2} + \underset{\underset{S}{\diagdown\diagup}}{C_6H_5CH\text{——}CH_2}$$
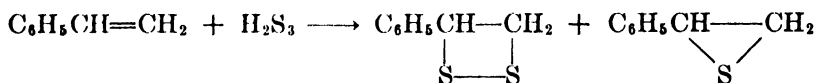
Styrene has been reported to give an addition product with ethyl mercaptan (420). The addition of thiophenol proceeded contrary to Markownikoff's rule to give phenyl β-phenethyl thioether (565) in 90 per cent (31) to 100 per cent yield (658). It has been suggested that the reaction proceeds by a free-radical mechanism (658). It is accelerated by light and stopped by bases.

Styrene also adds thioglycolic acid contrary to Markownikoff's rule (307).

$$C_6H_5CH=CH_2 + HSCH_2COOH \rightarrow C_6H_5(CH_2)_2SCH_2COOH$$

This reaction is catalyzed by ascaridole (373, 376) and by peroxides in general, since no reaction occurs *in vacuo* over hydroquinone (376). The addition of thioacetic acid to styrene likewise is abnormal (309).

$$C_6H_5CH=CH_2 + CH_3COSH \rightarrow C_6H_5(CH_2)_2SCOCH_3$$

In the presence of iodine in anhydrous ether styrene added the following disulfides: dimethyl (75 per cent yield) (311), diethyl (72 per cent yield) (311),

$$C_6H_5CH=CH_2 + R_2S_2 \xrightarrow[\text{ether}]{I_2} \underset{\underset{SR}{|}}{C_6H_5CHCH_2SR}$$
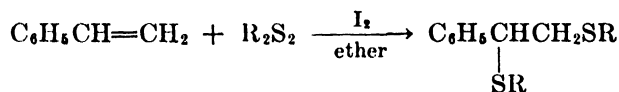
diphenyl (75 per cent yield) (311), dithiodiglycolic acid (310) (69 per cent yield, 311), and ethyl dithioglycolate (73 per cent yield) (311). Tri- and tetra-thiodiglycolic acids gave tarry products and diacetyl disulfide did not react (311).

Styrene reacted with sulfur monochloride to give di(β-phenyl-β-chloro)ethyl sulfide and sulfur (564). Treatment of this compound with sodium sulfide in alcohol gave diphenyl dithiane (270). With sodium β-naphthoxide in alcohol the product was distyryl sulfide, which decomposed before distillation (564).

$$C_6H_5CH{=}CH_2 + S_2Cl_2 \longrightarrow (C_6H_5CHClCH_2)_2S + S$$

Na₂S / alcohol

β-C₁₀H₇ONa / alcohol

$$[(C_6H_5CH{=}CH)_2S]$$
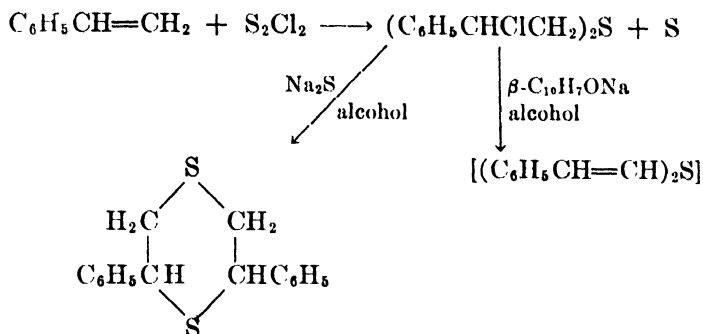
When the two were heated together, styrene and sulfur reacted to form an addition product (510). This was shown to be primarily 2,4-diphenylthiophene (57, 507) plus a little 2,5-diphenylthiophene and ethylbenzene (57).

Recently it has been found that styrene will undergo the Willgerodt reaction. With ammonium polysulfide at 210°C. the yield of phenylacetamide was 49 per cent (384), while the addition of pyridine (using sulfur and ammonium hydroxide) at the lower temperature of 165°C. raised this figure to 64 per cent (134). In a careful study of the reaction (385) the styrene and sulfur were boiled 2 hr. with different amines and then the resulting phenylthioacetamide hydrolyzed with 50 per cent sulfuric acid. The yields of phenylacetic acid obtained are listed after each amine: morpholine, 84 per cent; n-heptylamine, 59 per cent;
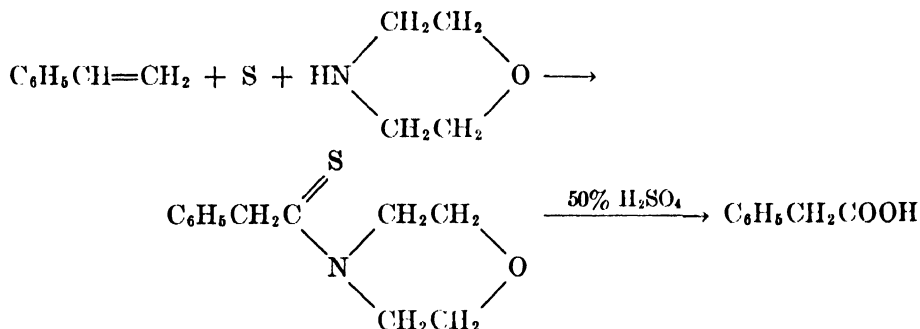
piperidine, 58 per cent; 2-ethylcyclohexylamine, 49 per cent; cyclohexylamine, 47 per cent; benzylamine, 34 per cent; aniline, 23 per cent; n-butylamine, 12.5 per cent; diethanolamine, 10.3 per cent; ethanolamine, 3.5 per cent. The morpholine modification was applied to substituted styrenes to obtain the following yields of substituted phenylacetic acids: o-chloro-, 63 per cent; p-chloro-, 59 per cent; 2,5-dichloro-, 61 per cent. When 2,5-dichlorostyrene was heated with sulfur and ammonium hydroxide 11 per cent of 2,5-dichlorophenylacetamide was obtained. Finally, the treatment of styrene with sulfur and ammonium hydroxide was found to give 61 per cent of phenylacetamide and 32 per cent of phenylacetic acid.

Several investigators have added thiocyanogen to styrene to give styrene

dithiocyanate (316, 364, 365, 690) and the reaction has been the subject of a number of patents (327, 333, 363). When the reaction was run in acetic acid solution and the thiocyanogen generated from sodium thiocyanate and bromine in the presence of the styrene, the yield was 65 per cent (365). A much better procedure was to generate the thiocyanogen from lead thiocyanate and bromine in benzene (690) or carbon tetrachloride (364) and then add the styrene. The yields were 80 and 87 per cent, respectively.

Styrene dithiocyanate also has been prepared by boiling an alcoholic solution of styrene dibromide and potassium thiocyanate (529). It can be nitrated in the para position.

X. REACTIONS WITH OXYGENATED SULFUR COMPOUNDS

Styrene reacts with sulfur dioxide in the presence of ascaridole to give a polymer (270, 643).

Treatment of styrene with sodium bisulfite at 100–140°C. gave mostly polystyrene (288) plus a trace of addition (429, 512). With ammonium bisulfite at 25°C. the product, obtained in 16 per cent yield, was formulated first as ethylbenzene-α-sulfonic acid (31). Subsequently it was shown that, in the addition of sulfites, the sulfur becomes attached to the β-carbon atom (373). That this addition is catalyzed by oxygen was shown by treating styrene with ammonium sulfite at 25°C. and 1 mm. pressure and also at 25°C. with air bubbled into the mixture (374). In the first case there was 2 per cent of addition, in the second 50 per cent. With sodium bisulfite in the presence of oxygen the principal product was shown to be sodium β-phenyl-β-hydroxyethanesulfonate plus smaller quantities of sodium β-styrylsulfonate and sodium β-phenylethanesulfonate (377). Sodium β-phenyl-β-hydroxyethanesulfonate also has been prepared by treating styrene bromohydrin (377, 721) or iodohydrin (377) with sodium sulfite. Some of its chemistry is illustrated by the following equations:

$$C_6H_5CHOHCH_2Br \xrightarrow[(377, 721)]{Na_2SO_3} \Big\langle \begin{array}{l} C_6H_5CHOHCH_2SO_3Na \\ C_6H_5(CH_2)_2SO_3Na \end{array}$$

$$\xrightarrow[(721)]{(CH_3CO)_2O} \; C_6H_5CHCH_2SO_3Na \;|\; OCOCH_3 \xrightarrow[(721)]{180-200°C.}$$

$$\xrightarrow{PCl_5 \; (377)} C_6H_5CH{=}CHSO_3Na$$

$$C_6H_5CH{=}CH_2 + NaHSO_3 \xrightarrow[(377)]{O_2} C_6H_5CH{=}CHSO_3Na$$
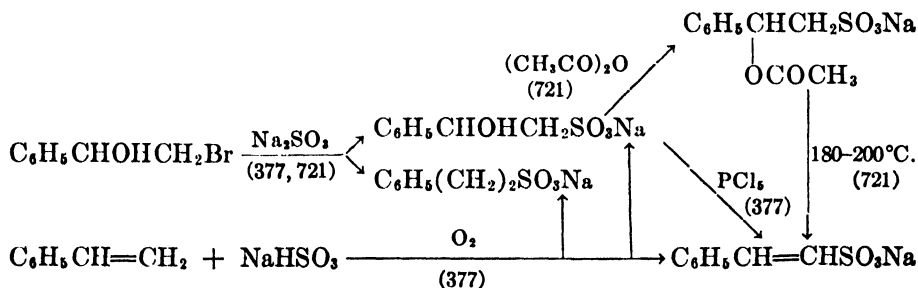
Styrene has been reported to add chlorosulfonic acid (322, 338). Sulfonation in the β-position has been effected by means of sulfamic acid (587) and by means of dioxane–sulfur trioxide (98, 720). At 2°C. the products isolated after neutralization were 19–26 per cent of sodium β-styrylsulfonate, 66–76 per cent of sodium β-phenyl-β-hydroxyethanesulfonate, and 6–10 per cent of distyrene sultone; whereas at 54.4°C. 74–75 per cent of sodium β-styrylsulfonate, 22–24 per cent of sodium β-phenyl-β-hydroxyethanesulfonate, and 3–5 per cent of distyrene

sultone were obtained (97a). In the following equations are shown some of the reactions of sodium β-styrylsulfonate:

$$C_6H_5CH{=}CBrSO_3Na$$
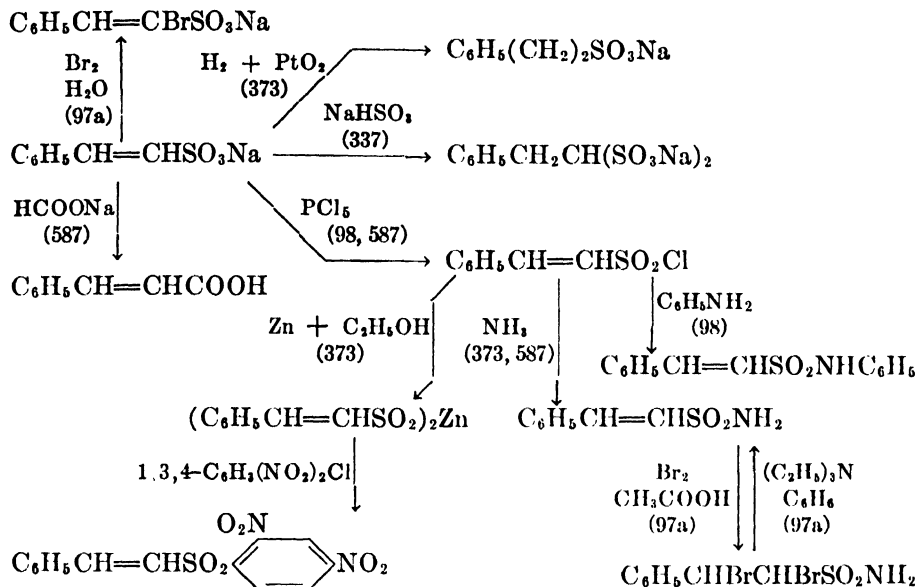
β-Bromostyrene also sulfonated in the β-position on treatment with the dioxane–sulfur trioxide complex (757a). The resulting sulfonic acid was converted to the amide by means of phosphorus pentachloride followed by ammonia.

XI. REACTIONS WITH NITROGEN COMPOUNDS

In the presence of sodium, styrene added di-n-butylamine to give 21 per cent of di-n-butyl-α-phenethylamine (149a).

β-Bromostyrene added ammonia (24 per cent yield) and piperidine (33 per cent yield) in ether solution at room temperature (456). An aniline addition of 5 per cent was obtained by boiling the two compounds for several days.

$$C_6H_5CH{=}CHBr \quad + \quad NH_3 \quad \rightarrow \quad C_6H_5\underset{\underset{NH_2}{|}}{C}HCH_2Br$$
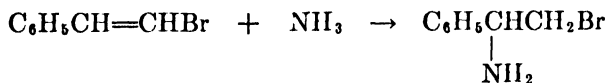
Neither styrene, β-bromostyrene, nor β-chlorostyrene added hydroxylamine (566).

The addition of amines to β-nitrostyrenes proceeds similarly to the addition of ammonia to β-bromostyrene. This reaction has been studied very extensively

$$C_6H_5CH{=}CHNO_2 \quad + \quad RNH_2 \quad \rightarrow \quad C_6H_5\underset{\underset{NHR}{|}}{C}HCH_2NO_2$$

by Worrall and the results of his many investigations are summarized in table 40. Included therein are hydrazines and other similar nitrogen compounds which also were examined.

TABLE 40
β-Nitrostyrenes and amines

SUBSTITUTED β-NITROSTYRENE	AMINE	ADDITION	REFERENCE
	Ammonia in alcohol	Polymerization	(789)
	Ammonia in benzene	2 moles	(789)
	Hydroxylamine	+	(566)
	Aniline	+	(789)
	p-Toluidine	+	(789)
	Phenylhydrazine	+	(526, 789)
	N,N-Diphenylhydrazine	+	(789)
	β-Naphthylhydrazine	+	(789)
	p-Tolylhydrazine	+	(789)
	Semicarbazide	+	(789)
	Thiosemicarbazide	+	(789)
	Piperidine	+	(789)
	Acetanilide	−	(789)
	N-Methylaniline	−	(789)
	N,N-Dimethylaniline	−	(789)
	o-Nitroaniline	−	(789)
	m-Nitroaniline	−	(789)
	p-Nitroaniline	−	(789)
	p-Chloroaniline	−	(789)
	p-Aminobiphenyl	−	(789)
	p-Aminophenol	−	(789)
	p-Phenetidine	−	(789)
	Ethyl *p*-aminobenzoate	−	(789)
	p-Aminoacetophenone	−	(789)
	p-Aminoacetophenone oxime	−	(789)
	Rosaniline	Polymerization	(789)
	o-Toluidine	−	(789)
	m-Toluidine	−	(789)
	α-Naphthylamine	−	(789)
	β-Naphthylamine	−	(789)
	p-Aminoazobenzene	−	(789)
	N-Methyl-*p*-aminoazobenzene	−	(789)
	N-Acetyl-*p*-phenylenediamine	−	(789)
	p-Bromophenylhydrazine	−	(789)
	p-Nitrophenylhydrazine	−	(789)
	α-Naphthylhydrazine	−	(789)
	Urea	−	(789)
	Thiourea	−	(789)
	o-Phenylenediamine	−	(789)
	m-Phenylenediamine	−	(789)
	Benzylamine	Polymerization	(789)
	N,N-Dimethyl-*p*-phenylenediamine	Polymerization	(789)
	N-Methyl-*N*-phenylhydrazine	Polymerization	(789)
	Guanidine	Polymerization	(789)

TABLE 40—*Continued*

SUBSTITUTED β-NITROSTYRENE	AMINE	ADDITION	REFERENCE
	Aminoguanidine	Polymerization	(789)
	Hydrazine	Polymerization	(789)
	p-Phenylenediamine	2 moles	(789)
	Benzidine	2 moles	(789)
β-Bromo.................{	Aniline	Decomposition	(788)
	o-Toluidine	+	(788)
	m-Toluidine	+	(788)
	p-Toluidine	+	(788)
	Phenylhydrazine	+	(788)
	β-Naphthylamine	Decomposition	(788)
	Diphenylamine	—	(788)
	m-Nitroaniline	—	(788)
	N.N-Dimethylaniline	—	(788)
p-Methyl.................{	Ammonia in alcohol	Polymerization	(790)
	Aniline	—	(790)
	p-Toluidine	—	(790)
	Phenylhydrazine	—	(790)
p-Methyl-β-chloro........{	Ammonia	—	(790)
	p-Toluidine	—	(790)
	p-Phenylenediamine	—	(790)
p-Methyl-β-bromo.........{	Ammonia	—	(790)
	p-Toluidine	—	(790)
	p-Phenylenediamine	—	(790)
3-Nitro-4-methyl..........{	Ammonia in benzene	2 moles	(790)
	Aniline	+	(790)
	p-Toluidine	+	(790)
	p-Phenylenediamine	2 moles	(790)
3-Nitro-4-methyl-β-chloro..{	Ammonia	—	(790)
	Aromatic amines	—	(790)
3-Nitro-4-methyl-β-bromo..{	Ammonia	—	(790)
	Aromatic amines	—	(790)
o-Fluoro-β-bromo..........{	p-Phenylenediamine	2 moles	(795)
	Benzidine	2 moles	(795)
2-Fluoro-5-nitro...........{	Aniline	+	(795)
	m-Toluidine	+	(795)
	p-Toluidine	∟	(795)
	Phenylhydrazine	+	(795)
	Benzidine	2 moles	(795)
	o-Toluidine	—	(795)
	Hydroxylamine	—	(795)
	p-Tolylhydrazine	—	(795)

TABLE 40—*Continued*

SUBSTITUTED β-NITROSTYRENE	AMINE	ADDITION	REFERENCE
2-Fluoro-5-nitro—*Continued*	Ammonia	—	(795)
	o-Anisidine	—	(795)
	m-Anisidine	—	(795)
	p-Anisidine	—	(795)
o-Chloro............	p-Toluidine	—	(791)
	p-Phenylenediamine	2 moles	(791)
2-Chloro-5-nitro...........	o-Toluidine	+	(791)
	m-Toluidine	+	(791)
	p-Toluidine	+	(791)
	p-Anisidine	+	(791)
	Phenylhydrazine	+	(791)
	p-Tolylhydrazine	+	(791)
	Ammonia	2 moles	(791)
	p-Phenylenediamine	2 moles	(791)
	Benzidine	2 moles	(791)
	Aniline	—	(791)
	m-Anisidine	—	(791)
	β-Naphthylamine	—	(791)
	β-Naphthylhydrazine	—	(791)
	m-Tolylhydrazine	—	(791)
	m-Phenylenediamine	—	(791)
	Hydroxylamine	Decomposition	(791)
	Hydrazine	Decomposition	(791)
	Piperidine	Decomposition	(791)
2-Chloro-5-nitro-β-bromo..	Aniline	—	(791)
	m-Toluidine	—	(791)
	p-Toluidine	+	(791)
	p-Phenylenediamine	2 moles	(791)
o-Bromo....	p-Toluidine	—	(794)
	p-Phenylenediamine	2 moles	(794)
2-Bromo-5-nitro...........	o-Toluidine	+	(794)
	m-Toluidine	+	(794)
	p-Toluidine	+	(794)
	o-Anisidine	+	(794)
	m-Anisidine	+	(794)
	p-Anisidine	+	(794)
	p-Phenetidine	+	(794)
	N,N-Dimethyl-p-phenyl-enediamine	+	(794)
	Phenylhydrazine	+	(794)
	Ammonia	2 moles	(794)
	p-Phenylenediamine	2 moles	(794)
	Benzidine	2 moles	(794)

TABLE 40—*Continued*

SUBSTITUTED β-NITROSTYRENE	AMINE	ADDITION	REFERENCE
β,2-Dibromo-5-nitro.......	*p*-Toluidine	+	(794)
	p-Phenylenediamine	2 moles	(794)
	Aniline	+	(793)
	o-Toluidine	+	(793)
	m-Toluidine	+	(793)
	p-Toluidine	+	(793)
	o-Anisidine	+	(793)
	m-Anisidine	+	(793)
2-Iodo-5-nitro	*p*-Anisidine	+	(793)
	Phenylhydrazine	+	(793)
	β-Naphthylhydrazine	+	(793)
	Hydroxylamine	+	(793)
	Semicarbazide	+	(793)
	Ammonia	2 moles	(793)
2-Iodo-5-nitro-β-bromo......	*p*-Toluidine	+	(793)
o-Nitro.................	*p*-Toluidine	−	(792)
	p-Phenylenediamine	2 moles	(792)
m-Nitro.................	*p*-Toluidine	−	(792)
	p-Phenylenediamine	2 moles	(792)
p-Nitro.................	*p*-Toluidine	−	(792)
	p-Phenylenediamine	2 moles	(792)
	Phenylhydrazine	+	(526)
2-Methoxy-4-nitro.........	*p*-Toluidine	−	(792)
	p-Phenylenediamine	2 moles	(792)
2-Nitro-4-chloro...........	*p*-Toluidine	+	(792)
	p-Phenylenediamine	2 moles	(792)
p-Chloro.................	*p*-Toluidine	−	(792)
	p-Phenylenediamine	−	(792)
o-Methoxy...............	*p*-Toluidine	−	(792)
	p-Phenylenediamine	−	(792)
p-Methoxy...............	*p*-Toluidine	−	(792)
	p-Phenylenediamine	−	(792)
	Phenylhydrazine	+	(526)
2,4-Dimethoxy............	*p*-Toluidine	−	(792)
	p-Phenylenediamine	−	(792)
3,4-Dimethoxy.............	Phenylhydrazine	+	(526)
2-Nitro-4-methoxy.........	*p*-Toluidine	−	(792)
	p-Phenylenediamine	−	(792)

TABLE 40—*Concluded*

SUBSTITUTED β-NITROSTYRENE	AMINE	ADDITION	REFERENCE
2,4-Dimethoxy-6-nitro	p-Toluidine	–	(792)
	p-Phenylenediamine	–	(792)
3-Methoxy-4-hydroxy	p-Toluidine	–	(792)
	p-Phenylenediamine	–	(792)
3,4-Methylenedioxy	p-Toluidine	–	(792)
	p-Phenylenediamine	–	(792)
	Phenylhydrazine	+	(526)

p-Methyl-β-nitrostyrene was decomposed by amylamine and by p-phenylene-diamine to nitromethane and the Schiff's base corresponding to the amine (790).

$$H_3C\text{—}\langle\rangle\text{—}CH{=}CHNO_2 \ + \ C_5H_{11}NH_2 \ \rightarrow$$

$$CH_3NO_2 \ + \ H_3C\text{—}\langle\rangle\text{—}CH{=}NC_5H_{11}$$
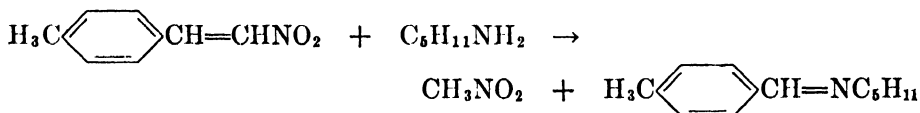
This same reaction was observed between β-nitrostyrene and p-methoxy-β-nitrostyrene and hydrazine (526). β-Bromo-β-nitrostyrene behaved similarly with p-phenylenediamine, benzidine, and N,N-diphenylhydrazine and with phenylhydrazine in boiling ethanol (788). The same reaction occurred between phenylhydrazine and p-methoxy-β-bromo-β-nitrostyrene and 3-methoxy-4-hydroxy-β-nitrostyrene (526).

The addition product of β-bromo-β-nitrostyrene and p-toluidine was decomposed by hot concentrated hydrochloric acid as follows (788):

$$C_6H_5CHCHBrNO_2 \ \xrightarrow[\text{concd. HCl}]{\text{heat}}$$
$$\overset{|}{NH}\text{—}\langle\rangle\text{—}CH_3$$

$$C_6H_5CHO \ + \ CH_2BrNO_2 \ + \ H_3C\text{—}\langle\rangle\text{—}NH_2{\cdot}HCl$$
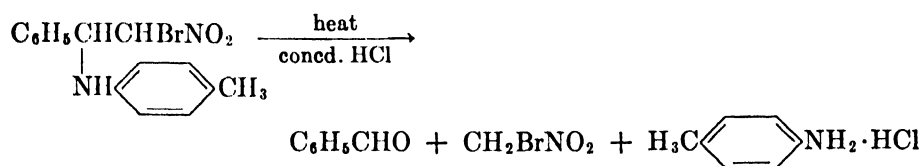
Pyrolysis of the phenylhydrazine addition products of β-nitrostyrene, p-methoxy-β-nitrostyrene, 3,4-dimethoxy-β-nitrostyrene, 3,4-methylenedioxy-β-nitrostyrene, and β,p-dinitrostyrene gave nitromethane and the phenylhydrazone of the corresponding aromatic aldehyde (526).

$$C_6H_5CHCH_2NO_2 \ \xrightarrow{160{-}180°C.} \ C_6H_5CH{=}NNHC_6H_5 \ + \ CH_3NO_2$$
$$\overset{|}{NHNHC_6H_5}$$
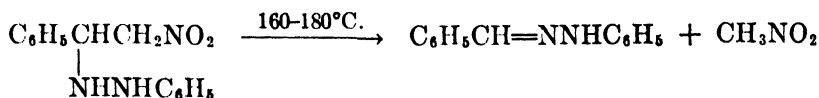
Selenium dioxide oxidation of the phenylhydrazine addition product of β,p-dinitrostyrene gave the phenylhydrazone of β,p-dinitroacetophenone.

When styrene was heated with phenylhydrazine some benzaldehyde phenyl-hydrazone was isolated (545). The yields of quaternary salts from β-bromo-

styrene and pyridine or quinoline were too low for the reactions to be of preparative value (287).

Styrene added trichloroamine and the addition product reacted with hydrogen chloride in carbon tetrachloride to give a 28 per cent yield based on styrene of β-chloro-α-phenethylamine (142, 143).

$$C_6H_5CH=CH_2 + NCl_3 \rightarrow C_6H_5\underset{\underset{NCl_2}{|}}{C}HCH_2Cl \xrightarrow{HCl} C_6H_5\underset{\underset{NH_2}{|}}{C}HCH_2Cl + 2Cl_2$$
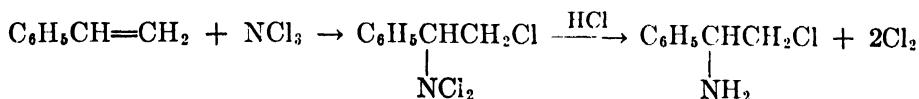
The addition of N,N-dibromo-p-toluenesulfonamide proceeded similarly (375). With N-alkyl-N-bromosulfonamides the mode of addition was reversed, so that the nitrogen became attached to the β-carbon atom. This was true for the addition of the following N-bromosulfonamides to styrene (375): N-methylbenzene, N-methyl-p-toluene, N-benzyl-p-toluene, N-benzylbenzene, $N,β$-phenethyl-p-toluene, and N-($α$-phenyl-$β$-bromoethyl)-p-toluene; and for the addition of N-methyl-N-bromo-p-toluenesulfonamide to p-fluorostyrene (229).

β-Aminosytrenes have been prepared by distilling the corresponding diamines derived from phenylacetaldehyde (470). This method has been applied to β-diethylamino-, β-piperidino-, β-methylbenzylamino-, and β-dibenzylamino-styrenes.

$$C_6H_5CH_2CH[N(C_2H_5)_2]_2 \xrightarrow{distil} C_6H_5CH=CHN(C_2H_5)_2 + (C_2H_5)_2NH$$

Both β-methylphenylamino- and β-methyl-p-tolylamino-styrene have been prepared by heating phenylacetaldehyde acetal with the appropriate amine (500). The p-toluenesulfonamides of β-(N-methylamino)styrene and β-(N-benzylamino)styrene were prepared by dehydrohalogenating the p-toluenesulfonamides of the corresponding β-phenyl-β-bromoethylamines (375).

Both acetophenone ketal and p-methylacetophenone ketal were treated with methylaniline, ethylaniline, methyl-p-toluidine, and methyl-p-anisidine at 140–240°C. to give 50–85 per cent of the corresponding α-aminostyrenes (300).

$$\underset{\underset{(OC_2H_5)_2}{||}}{C_6H_5C}CH_3 + C_6H_5NHCH_3 \rightarrow C_6H_5\underset{\underset{CH_3NC_6H_5}{|}}{C}=CH_2$$
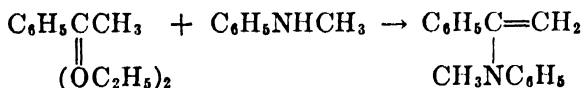
The hydrogenation of these compounds has been mentioned previously. β-Methylaminostyrene has been postulated as an intermediate in the formation of 1,3,5-triphenylbenzene from phenylacetylene and methylamine at 260°C. (419).

Benzamide reacted with β-bromostyrene, p-methoxy-β-bromostyrene, and 3,4-methylenedioxy-β-bromostyrene in the presence of copper acetate and potassium carbonate in boiling cymene to give the corresponding β-benzamino-styrene (628). That from β-bromostyrene was converted to the corresponding isoquinoline by boiling in decalin in the presence of alumina.

$$C_6H_5CH{=}CHBr \xrightarrow{C_6H_5CONH_2} C_6H_5CH{=}CHNHCOC_6H_5$$
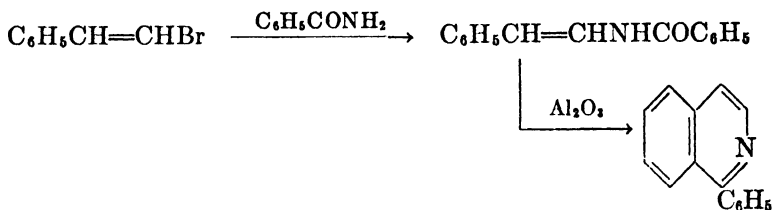
β-Bromostyrene also reacted with potassium phthalimide to give a 60 per cent yield of β-phthalimidostyrene. This compound added hydrogen bromide and was partly hydrolyzed by cold alcoholic potassium hydroxide.
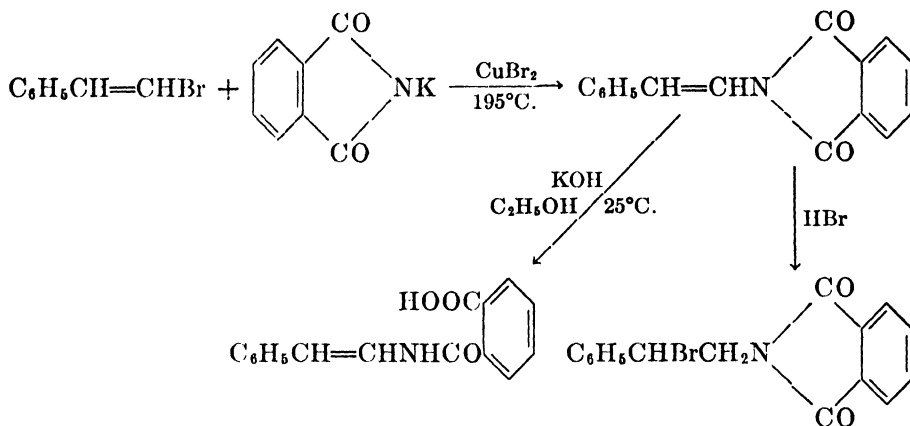
Styrene first was reported to have coupled with diazotized p-nitroaniline (735), but a later paper stated that neither styrene nor dimethylstyrene coupled with either diazotized p-nitroaniline or diazotized 2,4-dinitroaniline (734). In alcohol solution 2,4-dinitrobenzenediazonium sulfate reacted with p-methoxystyrene to give anisaldehyde 2,4-dinitrophenylhydrazone and with styrene to give a small amount of unidentified product (7). α-Ethoxystyrene was reported to react instantly with benzenediazonium acetate in acetic acid (508). Styrene added diazomethane to give a dihydropyrazole (537). At low temperatures
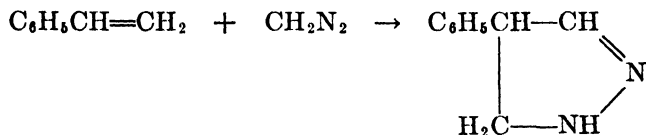
styrene did not react with ethyl diazoacetate to give a pyrazole (128). At 100°C. 33 per cent of the substituted cyclopropane was obtained (129). With p-nitro-

styrene the yield was 83.5 per cent (477a).
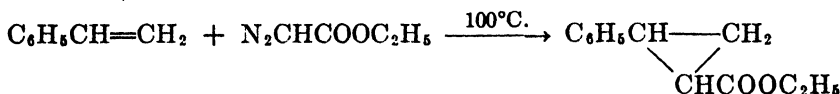
β-Nitrostyrene reacted with ethyl diazoacetate to give an unstable dihydropyrazole which lost nitrous acid (400).

$$C_6H_5CH=CHNO_2 + N_2CHCOOC_2H_5 \rightarrow$$

$$\left[\begin{array}{c} C_6H_5CH\text{---}CHNO_2 \\ | \quad\quad | \\ C_2H_5OCOC \quad NH \\ \diagdown\diagup \\ N \end{array}\right] \xrightarrow{-HNO_2} \begin{array}{c} C_6H_5C=\!\!=\!\!=CH \\ | \quad\quad | \\ C_2H_5OCOC \quad NH \\ \diagdown\diagup \\ N \end{array}$$
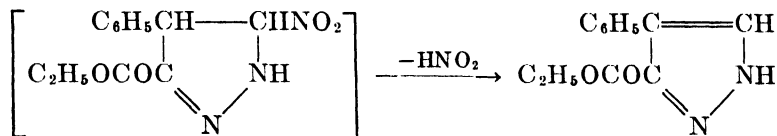
With phenylazide styrene gave a dihydrotriazole (784).

$$C_6H_5CH=CH_2 + C_6H_5N_3 \rightarrow C_6H_5\overset{\displaystyle NC_6H_5}{\underset{\displaystyle H_2C\text{---}N}{\underset{|}{CH}}\diagdown N}$$
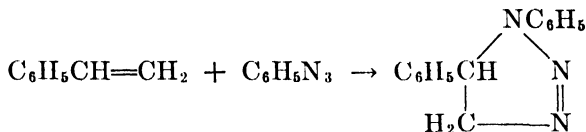
Styrene reacted with nitrosyl chloride to give a nitrosochloride, which decomposed on heating or treatment with alcoholic potassium hydroxide (748). By-products of the reaction were styrene dichloride and β-nitrostyrene (555). When the reaction was conducted at $-30°$C., the yield of nitrosochloride was 30 per cent (556). It reacted with piperidine to give a nitrolpiperidine. Early attempts to prepare nitrosochlorides from p-methylstyrene, p-ethylstyrene, and 2,4,6-trimethylstyrene were unsuccessful (389). Later, at 25°C., only p-methyl-β-chlorostyrene was obtained from the reaction between p-methylstyrene and nitrosyl chloride (555). At $-60°$C. an 80 per cent yield of nitrosochloride was obtained, from which a nitrolpiperidine was prepared (556). At $-10°$C. β-bromostyrene reacted with nitrosyl chloride to give a nitrosochloride from which a nitrolpiperidine was prepared. Heating of this nitrosochloride with alcoholic hydrogen chloride gave hydroxylamine hydrochloride. All six of these nitrosochlorides and nitrolpiperidines were believed to be partly dimeric (556). When treated with nitrosyl chloride, β-chlorostyrene and β-nitrostyrene gave difficultly separable mixtures (555). α-Chlorostyrene reacted to give trichlorostyrene and β-nitrodichlorostyrene.

$$C_6H_5CCl=CH_2 + NOCl_2 \rightarrow C_6H_5CCl=CCl_2 + C_6H_5CCl=CClNO_2$$

Styrene added nitrosobenzene to give an unstable adduct which decomposed to give phenylhydroxylamine, formaldehyde, and diphenylnitrone (347).

$$C_6H_5CH=CH_2 + C_6H_5NO \rightarrow \left[\begin{array}{c} NC_6H_5 \\ \diagup \quad \diagdown \\ C_6H_5CH \quad\quad O \\ | \quad\quad\quad | \\ H_2C \quad\quad NC_6H_5 \\ \diagdown \quad \diagup \\ O \end{array}\right] \rightarrow$$

$$C_6H_5NHOH + HCHO + C_6H_5CH=\underset{\displaystyle \underset{O}{\downarrow}}{NC_6H_5}$$
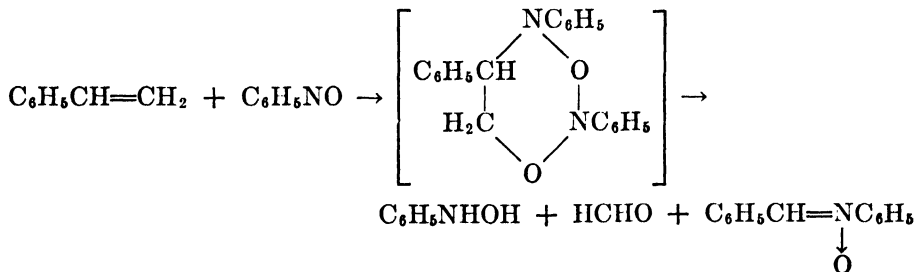
Phenyl-*p*-chlorophenylnitrone was isolated from the reaction between styrene and *p*-chloronitrosobenzene. Styrene reacted with nitrobenzene to give diphenylnitrone, azobenzene, formic acid, benzaldehyde, and benzoic acid (12).

Tönnies (754, 755) first effected the addition of N_2O_2 to styrene by treating the compound with potassium nitrite in acetic acid. The product gave β-nitrostyrene on treatment with sulfuric acid, was reduced to a compound having the empirical formula of phenylethanolamine, and reacted with aniline, ammonia, or methylamine (756). Sommer (691) treated styrene with nitrogen trioxide in ether to obtain β-nitrostyrene and an N_2O_3 addition product which he called α-styrene nitrosite. Heating in ethanol converted α-styrene nitrosite to an isomeric β-styrene nitrosite. When the α-styrene nitrosite was heated dry, the products were β-nitrostyrene, benzonitrile, nitric oxide, carbon dioxide, and water (692). The β-styrene nitrosite gave all but the β-nitrostyrene under the same conditions. When β-styrene nitrosite was treated with concentrated hydrochloric acid, a compound was formed which Sommer postulated as α-nitrophenylacetaldehyde. The aniline reaction product of α-styrene nitrosite was formulated as β,*N*-diphenyl-β-nitroethylamine. Sommer believed that β-styrene nitrosite had one of the two alternate formulas shown below and that α-styrene nitrosite was a dimer of the β-isomer.

$$\underset{\underset{NO}{|}}{C_6H_5CHCH_2NO_2} \quad \text{or} \quad \underset{\underset{NO_2}{|}}{C_6H_5CHCH_2NO}$$
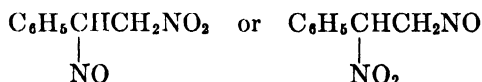
Wieland (775) raised the yield of α-styrene nitrosite to 70–80 per cent by using nitrogen trioxide in ether. The conversion of the α-form to the β-form was quantitative. Wieland believed β-styrene nitrosite to be ω-nitroacetophenone oxime, since it gave ω-nitroacetophenone with concentrated hydrochloric acid in the cold (Sommer had postulated the nitroaldehyde) and benzonitrile, carbon dioxide, and hydroxylamine with hot concentrated hydrochloric acid. The α-styrene nitrosite was postulated as a dimer which underwent the following reactions:

$$\underset{\underset{N_2O_2}{|}}{C_6H_5CHCH_2NO_2} \quad \overset{C_6H_5NH_2}{\underset{NaOH}{\Big\langle}} \quad \begin{array}{l} \underset{\underset{NHC_6H_5}{|}}{C_6H_5CHCH_2NO_2} \quad + \quad NO \\[2em] N_2O \;+\; H_2O \;+\; C_6H_5CHO \;+\; CH_3NO_2 \end{array}$$

$$C_6H_5CHCH_2NO_2$$
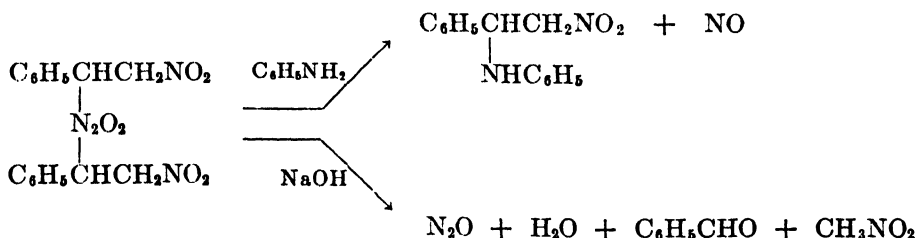
The corresponding structures were given for the nitrosites from *p*-methoxystyrene and nitrogen trioxide (778). In this case the α-nitrosite gave β-nitro-*p*-methoxystyrene on heating with alcoholic potassium hydroxide.

α-Ethoxystyrene reacted instantly with nitrous acid (508).

In benzene solution styrene added NO_2Cl in low yield (707).

$$C_6H_5CH{=}CH_2 \;+\; NO_2Cl \quad \xrightarrow{\;C_6H_6\;} \quad \underset{\underset{NO_2}{|}}{C_6H_5CHCH_2Cl}$$
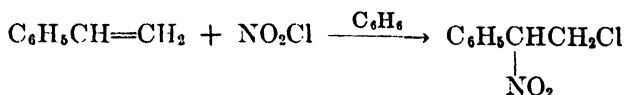
In ether the pseudonitrosite was obtained. In ether solution phenylacetylene gave β-chloro-α-nitrostyrene.

As early as 1839 Simon (673) obtained β-nitrostyrene in low yield by distilling styrene with nitric acid. Kopp (411) and Blyth and Hofmann (87) repeated the experiment shortly thereafter. Boiling styrene with concentrated nitric acid gave nitrobenzoic acid (87, 411) as well as benzaldehyde and benzoic acid (87). When Sommer (691) treated styrene with potassium nitrate in acetic acid, α-styrene nitrosite and a variety of other nitration products were obtained. Treatment of styrene with nitrogen pentoxide in ether gave a 28 per cent yield of β-nitrostyrene (571).

Isopropylstyrene reacted vigorously with fuming nitric acid to give a tar (551). Treatment of β-bromostyrene with fuming nitric acid gave 37 per cent of β,p-dinitro-β-bromostyrene, 20 per cent of β,o-dinitro-β-bromostyrene, and a little p-nitrobenzoic acid (224).

$$C_6H_5CH{=}CHBr \xrightarrow[\text{HNO}_3]{\text{fuming}} O_2N\!\!\left\langle\underline{\quad}\right\rangle\!\!CH{=}CBrNO_2 \; +$$

$$\left\langle\underline{\quad}\right\rangle\!\!CH{=}CBrNO_2 \; + \; O_2N\!\!\left\langle\underline{\quad}\right\rangle\!\!COOH$$
$$\quad\;\; NO_2$$
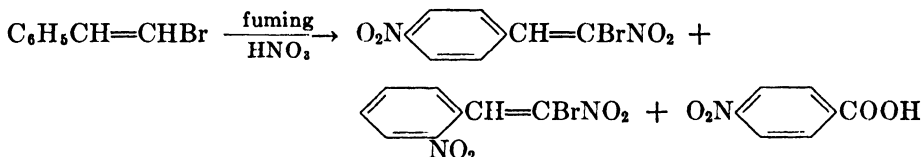
Early investigators reported the nitration of β-nitrostyrene with fuming nitric acid as giving mostly β,p-dinitrostyrene and some β,o-dinitrostyrene (571, 737). At $-15°$ to $-10°C$. a 95.3 per cent yield of dinitro compounds was obtained (46). By oxidation with potassium permanganate to the corresponding nitrobenzoic acids, the mixture was shown to be 67 per cent para, 30 per cent ortho, and <2 per cent meta.

When the 2-position in β-nitrostyrene is substituted by halogen, treatment with fuming nitric acid places the second nitro group in the 5-position. This has been shown to be true for 2-fluoro- (795), 2-chloro- (791, 794), 2-bromo- (794), and 2-iodo-β-nitrostyrenes (793). Nitration of o-methoxy-β-nitrostyrene has

$$\left\langle\underline{\quad}\right\rangle\!\!CH{=}CHNO_2 \xrightarrow[\text{HNO}_3]{\text{fuming}} \overset{O_2N}{\left\langle\underline{\quad}\right\rangle}\!\!CH{=}CHNO_2$$
$$\quad F \qquad\qquad\qquad\qquad\qquad F$$
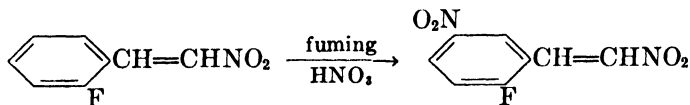
been reported to give 2-methoxy-β,4-dinitrostyrene, and nitration of p-methoxy-β-nitrostyrene gave 4-methoxy-β,2-dinitrostyrene (792).

Treatment of styrene with silver nitrate, pyridine, and chlorine in chloroform gave a product containing 22.9 per cent chlorine (760). $ClNO_3$ was believed to be an intermediate in this reaction.

Treatment of m,β-dinitrostyrene (243) or p,β-dinitrostyrene (244) with concentrated sulfuric acid gave the corresponding aldoxime and carbon monoxide.

$$\left\langle\underline{\quad}\right\rangle\!\!CH{=}CHNO_2 \xrightarrow[\text{H}_2\text{SO}_4]{\text{concd.}} \left\langle\underline{\quad}\right\rangle\!\!CH{=}NOH \; + \; CO$$
$$O_2N \qquad\qquad\qquad\qquad\qquad O_2N$$
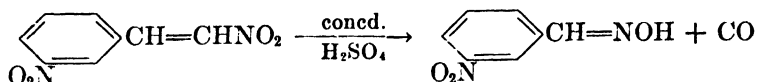
4-Amino-β,2-dinitrostyrene gave off carbon monoxide on heating with concentrated sulfuric acid (243). When β-nitrostyrene was heated with more dilute

sulfuric acid, benzaldehyde, hydroxylamine, and carbon monoxide were obtained (571). With saturated hydrochloric acid β-nitrostyrene yielded α-chlorophenylacetic acid and hydroxylamine.

$$C_6H_5CH\!\!=\!\!CHNO_2 \xrightarrow{HCl} C_6H_5CHClCOOH + NH_2OH$$

β-Nitrostyrene reacted with potassium cyanide to give α- and β-forms of a dimeric product (306). Treatment of the α-form with hydrochloric acid at 145–155°C. gave diphenylchlorosuccinic acid.

$$2C_6H_5CH\!\!=\!\!CHNO_2 \xrightarrow[H_2O]{\substack{2KCN \\ C_2H_5OH}} 2\begin{bmatrix} C_6H_5CHCH\!\!=\!\!NO_2K \\ | \\ CN \end{bmatrix} \longrightarrow$$

$$\begin{bmatrix} C_6H_5CHCH\!\!=\!\!NO_2K \\ | \\ C_6H_5CCH\!\!=\!\!NO_2K \\ | \\ CN \end{bmatrix} \xrightarrow{CH_3COOH}$$

$$\begin{array}{cc} C_6H_5CHCH_2NO_2 & C_6H_5CHCOOH \\ | & | \\ C_6H_5CCH_2NO_2 \xrightarrow[145\text{-}155°C.]{HCl} C_6H_5CClCOOH \\ | \\ CN \end{array}$$
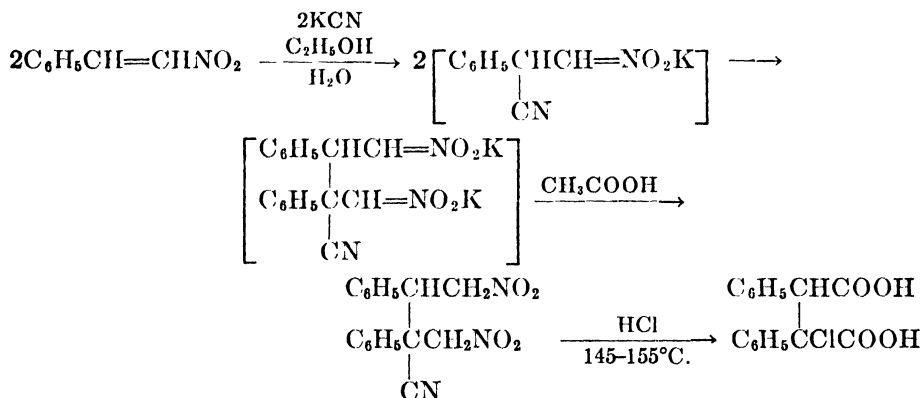
XII. PHOSPHORUS AND ARSENIC DERIVATIVES

Treatment of styrene with phosphorus pentachloride gave an addition product which reacted with water to produce styrenephosphonic acid (66, 285, 736).

$$C_6H_5CH\!\!=\!\!CH_2 + PCl_5 \rightarrow C_6H_5CHClCH_2PCl_4 \xrightarrow{H_2O} C_6H_5CH\!\!=\!\!CHPO_3H_2$$

This general method has been used to synthesize the substituted β-styrenephosphonic acids (412) listed in table 41. Under similar conditions α-chlorostyrene gave α-chlorostyrenephosphonic acid as well as considerable benzoic acid (67). α-Chlorostyrenephosphonic acid was obtained in 34 per cent yield by treating phenylacetylene with phosphorus pentachloride, followed by hydrolysis of the addition compound. Treatment with boiling aqueous potassium hydroxide gave phenylacetylenephosphonic acid.

$$\begin{array}{c} C_6H_5CCl\!\!=\!\!CH_2 \\ \diagdown \xrightarrow{PCl_5} C_6H_5CCl\!\!=\!\!CHPO_3H_2 \xrightarrow{KOH} C_6H_5C\!\!\equiv\!\!CPO_3H_2 \\ C_6H_5C\!\!\equiv\!\!CH \end{array}$$
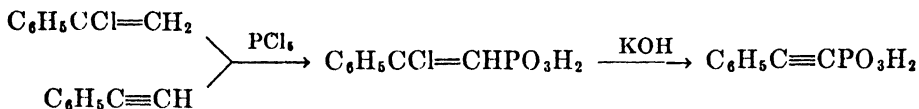
The following phenylacetylenes similarly were converted to α-chlorostyrenephosphonic acids; o-methoxy- (quantitative yield), p-methoxy- (64 per cent yield), and o-chloro- (49 per cent yield). The last two named were converted to the corresponding phenylacetylenephosphonic acids in 70 and 70 per cent yields, respectively.

Phosphorus pentabromide reacted differently from phosphorus pentachloride (68). With phenylacetylene 34 per cent of α,β-dibromostyrene was obtained, and with β-bromostyrene no reaction occurred.

Phenylacetylene reacted with arsenic trichloride to give 55 per cent of β-(α-chlorostyryl)dichloroarsine (350) as well as some bis-β-(α-chlorostyryl)chloroarsine (319). Treatment of the dichloroarsine with hot aqueous alcoholic sodium hydroxide gave the arsenious oxide (350). With aqueous alcoholic hydrogen peroxide an almost quantitative yield of the arsonic acid was obtained.

$$C_6H_5C\equiv CH + AsCl_3 \xrightarrow{110°C.} C_6H_5CCl\!=\!CHAsCl_2$$

$$C_6H_5CCl\!=\!CHAsO \qquad\qquad C_6H_5CCl\!=\!CHAsO(OH)_2$$

(left arrow: NaOH / H_2O-C_2H_5OH / 110-120°C.)

(right arrow: H_2O_2 / H_2O-C_2H_5OH)
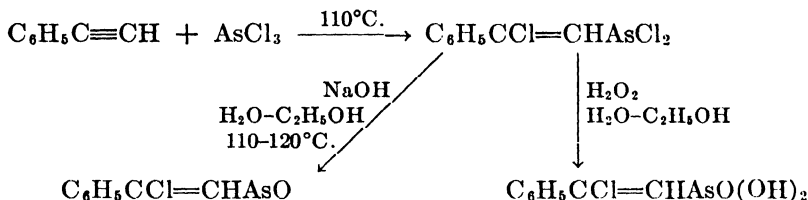
TABLE 41

β-Styrenephosphonic acids

β-STYRENEPHOSPHONIC ACID	YIELD
	per cent
2,4-Dimethyl	47
2,4,6-Trimethyl	55
p-Ethyl	39
o-$tert$-Butyl	33
p-$tert$-Butyl	47

β-Bromostyrene served as a source of arsenic derivatives, as shown by the following equations (153):

$$C_6H_5CH\!=\!CHBr \xrightarrow[C_2H_5OH]{Na_2HAsO_3} C_6H_5CH\!=\!CHAsO_3Na$$
(20 per cent)

$$(C_6H_5CH\!=\!CH)_3As$$
$$\downarrow CH_3I$$
$$[(C_6H_5CH\!=\!CH)_3AsCH_3]^+I^-$$

(arrow: AsCl$_3$ / Na / C$_6$H$_6$ / CH$_3$COOC$_2$H$_5$)

$$C_6H_5CH\!=\!CHBr \xrightarrow[(CH_3)_2AsBr]{Na, C_6H_6, CH_3COOC_2H_5} C_6H_5CH\!=\!CHAs(CH_3)_2$$

$$\xrightarrow[(CH_3)_2AsBr]{Mg, (C_2H_5)_2O}$$

$$\downarrow CH_3I$$
$$[C_6H_5CH\!=\!CHAs(CH_3)_3]^+I^-$$

$C_6H_5AsCl_2$ / aqueous NaOH

Cl$_2$ in CCl$_4$, then 185-190°C.
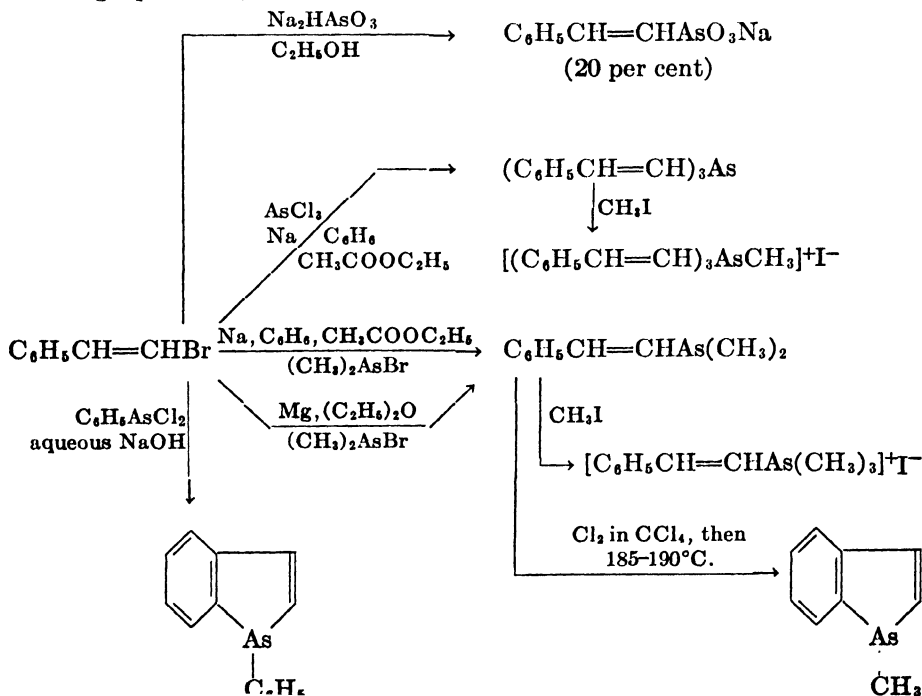
o-Vinylphenyldichloroarsine was cyclized by treatment with aluminum chloride in carbon disulfide (151, 152). The same product was obtained by treating tristyrylarsine with arsenic trichloride at 180°C. (153).
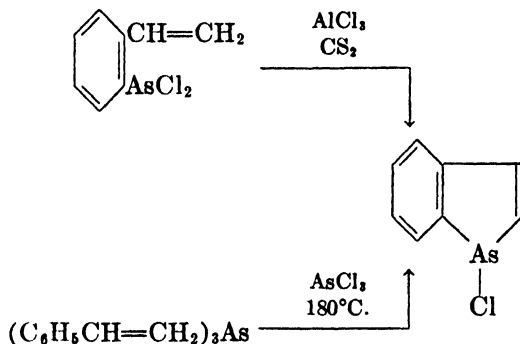
While β-bromostyrene gave a color with antimony trichloride in chloroform, styrene itself did not (646).

XIII. CHEMISTRY INVOLVING METALS

A. Alkali metals

When styrene was treated with ethyllithium in anhydrous ether followed by carbonation, a 1.7 per cent yield of α-phenylvaleric acid was obtained (261).

$$C_6H_5CH{=}CH_2 \ + \ C_2H_5Li \ \xrightarrow[\text{then CO}_2]{\text{ether}} \ CH_3(CH_2)_2\underset{\underset{C_6H_5}{|}}{C}HCOOH$$
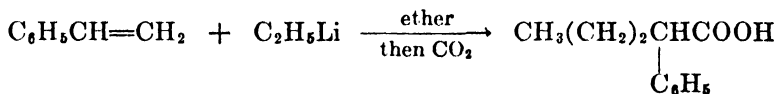
A metal adduct has been postulated as the intermediate in the reduction of styrene by lithium or sodium and secondary amines in ether solution (806a).

$$C_6H_5\underset{\underset{Li}{|}}{C}HCH_2Li$$
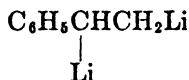
The reactions of β-chlorostyrene and β-bromostyrene with phenyllithium and with butyllithium have been considered in connection with those compounds.

β-Styryllithium, from β-bromostyrene and lithium, has been discussed in the section on β-bromostyrene chemistry.

In ether styrene was polymerized almost entirely by sodium (654). In liquid ammonia about 50 per cent of ethylbenzene was isolated along with polystyrene (787). The reactions of β-bromostyrene, styrene dibromide, α-chlorostyrene, and *p*-methyl-α-chlorostyrene with sodium in liquid ammonia have been discussed in connection with those compounds. Carbonation of the reaction product between α-bromostyrene and sodium gave a mixture of cinnamic and β-phenylpropionic acids (722).

Early investigators reported that sodiomalonic ester polymerized both styrene (293, 767) and β-nitrostyrene (293). Later, an 80 per cent yield of addition product was obtained with β-nitrostyrene (399).

$$C_6H_5CH\!=\!CHNO_2 + NaCH(COOCH_3)_2 \xrightarrow[HCl]{then} \underset{\underset{CH(COOCH_3)_2}{|}}{C_6H_5CHCH_2NO_2}$$
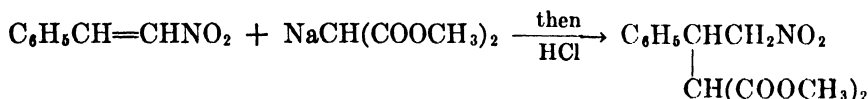
β-Bromostyrene did not react with the sodium derivatives of ethyl malonate, ethyl acetoacetate, or ethyl cyanoacetate (452).

Styrene reacted with potassium cumene to give the addition product shown below (805). This in turn added more styrene, depending on the ratio of the reactants in the reaction mixture.

$$C_6H_5CH\!=\!CH_2 + C_6H_5C(CH_3)_2K \rightarrow \underset{\underset{K}{|}}{C_6H_5CHCH_2C(CH_3)_2C_6H_5}$$
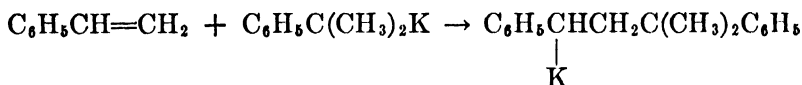
B. Magnesium

While it was reported originally that styrene reacted with phenylmagnesium bromide (144), it has been shown since that no reaction occurs with this reagent (536) even in boiling xylene (387). Ethylmagnesium iodide (536), methylmagnesium iodide (536), benzylmagnesium chloride (264), and triphenylmethylmagnesium chloride (264) likewise do not react with styrene.

The preparation and reactions of styrylmagnesium bromide have been discussed in detail in connection with the source material, β-bromostyrene.

While styrene did not react with ethylstrontium, with ethylbarium there was obtained upon carbonation a 0.6 per cent yield of α-phenylvaleric acid (261).

C. Mercury

The addition of mercuric acetate to styrene from aqueous solution was reported long before the structure of the product was established (468, 731). The compound proved to be β-hydroxy-β-phenethylmercuric acetate (534). With sodium chloride or sodium bromide the acetate group was replaced by the halogen in question. Treatment with sodium amalgam gave α-phenethyl alcohol.

$$C_6H_5CH\!=\!CH_2 \xrightarrow{(CH_3COO)_2Hg} C_6H_5CHOHCH_2HgOCOCH_3$$

NaX ↙   ↘ NaHg

$$C_6H_5CHOHCH_2HgX \qquad C_6H_5CHOHCH_3$$
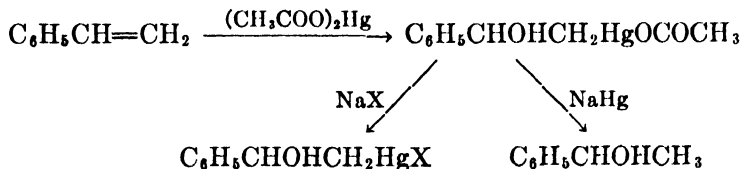
In acetic acid solution styrene reacted with mercuric acetate to give β-acetoxy-β-phenethylmercuric acetate (572). In methanol solution a 60 per cent yield of β-methoxy-β-phenethylmercuric acetate was obtained (796). Some of the reac-

tions of this compound are shown in the following equations:

$$C_6H_5CHCH_2HgOCOCH_3 \quad \xrightarrow{\quad C_6H_5COOH \quad} \quad C_6H_5CHCH_2HgOCOC_6H_5$$
$$\underset{\displaystyle OCH_3}{\big|} \qquad\qquad\qquad\qquad\qquad \underset{\displaystyle OCH_3}{\big|}$$

$$\xrightarrow{\quad KBr,\ CH_3OH,\ 0°C. \quad} \quad C_6H_5CHCH_2HgBr$$
$$\underset{\displaystyle OCH_3}{\big|}$$

(Almost quantitative yield; with BrCN, 50 per cent yield)

$$\xrightarrow{\quad\quad} \quad C_6H_5CHCH_2Br$$
$$\underset{\displaystyle OCH_3}{\big|}$$
$$Br_2,\ CH_3OH,\ 0°C.$$

(70 per cent yield)

$$\xrightarrow{\quad\quad} \quad C_6H_5CH{=}CH_2$$
boiling (CH₃CO)₂O, cold CH₃COCl, CH₃MgBr, or Na₂S₂O₃
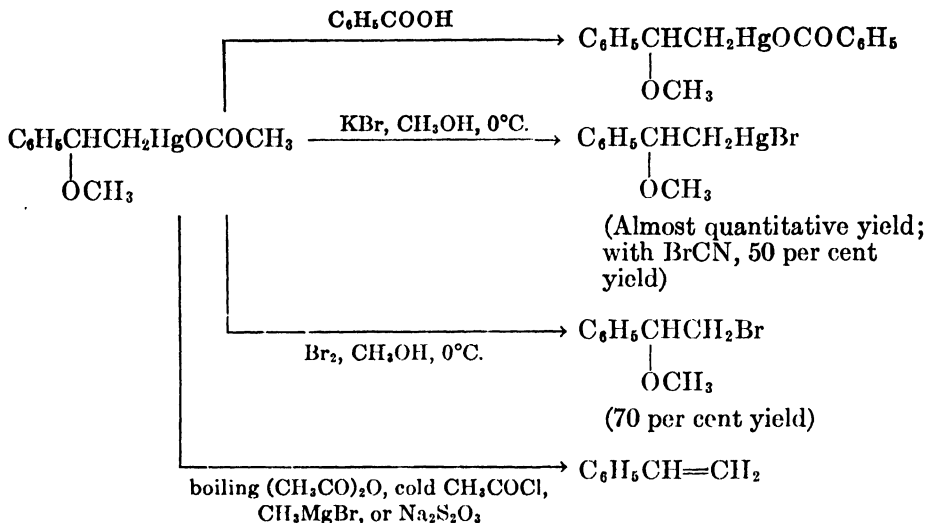
2,6-Dimethoxystyrene also added mercuric acetate from aqueous solution (667). The product was converted to β-(2,6-dimethoxyphenyl)-β-hydroxyethylmercuric chloride by means of aqueous potassium chloride and then the latter compound was reduced to α-(2,6-dimethoxyphenyl)ethyl alcohol by means of sodium amalgam and water.

β-Ethoxystyrene added mercuric acetate from aqueous solution (467) to give a compound of the following probable structure (534):

$$C_6H_5CHCH(OH)OC_2H_5$$
$$\underset{\displaystyle HgOCOCH_3}{\big|}$$
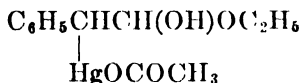
Treatment with dilute hydrochloric acid gave phenylacetaldehyde (467).

p-Methoxystyrene reacted with mercuric oxide and iodine in moist ether to give p-methoxyphenylacetaldehyde without the appearance of any intermediate iodohydrin or mercury compound (473).

Styrylmercuric chloride has been prepared by treating zinc styrylsulfinate with alcoholic mercuric chloride (373). The bromide was obtained in 36 per cent yield from the reaction between styrylmagnesium bromide and mercuric bromide in ether (797). The compound also was obtained, along with distyrylmercury, from β-bromostyrene and sodium amalgam in a mixture of xylene and ethyl acetate at 140°C. or from β-bromostyrene, mercuric chloride, and sodium in boiling benzene (153). Styrylmercuric bromide reacted with bromine and with iodine in chloroform to give 74 and 79 per cent yields of β-bromostyrene and of β-iodostyrene, respectively (797).

D. Miscellaneous

Styrene formed an addition compound with aluminum chloride (255).

Tristyrylbismuth (216), triphenylstyryllead (265), and styrylboric acid (504) have been prepared from styrylmagnesium bromide. As usual, diphenylbutadiene also was isolated from the reaction mixture (216, 265).

$$C_6H_5CH\text{=}CHMgBr \begin{cases} \xrightarrow{\text{BiCl}_3} (C_6H_5CH\text{=}CH)_3Bi \\ \xrightarrow[\text{ether}]{(C_6H_5)_3PbCl} (C_6H_5)_3PbCH\text{=}CHC_6H_5 \\ \quad (28 \text{ per cent}) \\ \xrightarrow{(i\text{-}C_4H_9O)_3B} C_6H_5CH\text{=}CHB(OH)_2 \end{cases}$$
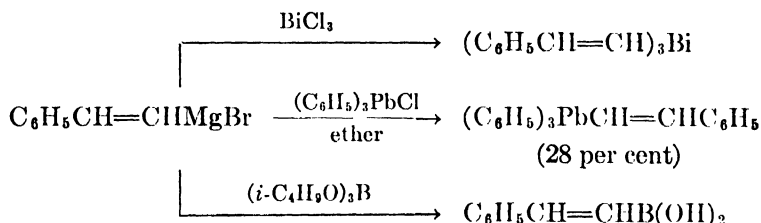
Styrene reacted with the addition compound of benzonitrile and palladous chloride in benzene to give a rather unstable compound $(C_6H_5CH\text{=}CH_2 \cdot PdCl_2)_2$ (378). Treatment of styrene with platinum tetrachloride or tetrabromide in glacial acetic acid gave similar compounds containing platinous chloride and platinous bromide, respectively (368). It has been suggested that all three of these products are a mixture of the two possible cyclic isomers (368, 378):

$$\begin{array}{c} \quad MX_2 \\ \diagup \quad \diagdown \\ C_6H_5CH \qquad CH_2 \\ | \qquad\qquad | \\ H_2C \qquad CHC_6H_5 \\ \diagdown \quad \diagup \\ \quad MX_2 \end{array} \quad \text{and} \quad \begin{array}{c} \quad MX_2 \\ \diagup \quad \diagdown \\ C_6H_5CH \qquad CHC_6H_5 \\ | \qquad\qquad | \\ H_2C \qquad CH_2 \\ \diagdown \quad \diagup \\ \quad MX_2 \end{array}$$
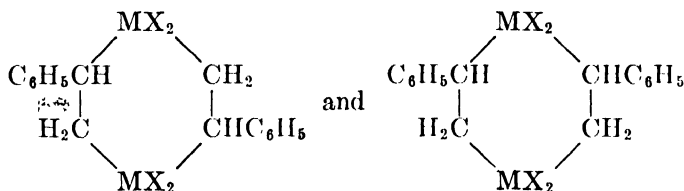
The platinous chloride compound also has been prepared by treating the corresponding ethylene adduct with styrene (23).

Styrene replaced ethylene, propylene, and butylene in their complexes with ammonium chloroplatinite (258).

$$NH_4(C_2H_4PtCl_3) + C_8H_8 \rightarrow NH_4(C_8H_8PtCl_3) + C_2H_4$$
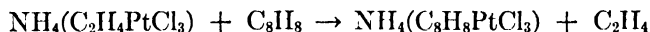
Styrene also reacted with metal chloroplatinites to give complexes (257) of the type $K(PtCl_3C_8H_8)$ (23). *Cis* and *trans* forms of the compound $PtC_8H_8NH_3Cl_2$ have been reported (257). While the *cis* form is insoluble in hydrochloric acid, the *trans* form dissolves to give the $NH_4(C_8H_8PtCl_3)$ mentioned above. Thiourea removed the styrene from either form. With ethylene adducts of metallic compounds somewhat more complicated products were obtained (23).

$$C_8H_8 + K[PtCl_3C_2H_4]H_2O \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{heat}} [Pt(NH_3)_4][PtCl_3C_8H_8]$$
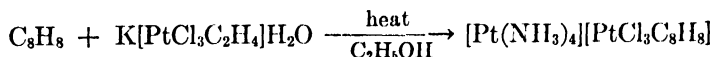
XIV. REACTIONS WITH ACID CHLORIDES, ETC.

In the presence of aluminum chloride in toluene solution styrene reacted with phosgene to give β-chlorophenylpropionyl chloride (541).

$$C_6H_5CH\text{=}CH_2 + COCl_2 \xrightarrow{\text{AlCl}_3} C_6H_5CHClCH_2COCl$$
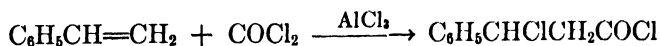
When refluxed for 24 hr. with oxalyl chloride, styrene yielded 9 per cent of cinnamoyl chloride (371).

Both acetyl chloride (432) and malonyl chloride (766) in the presence of stannic chloride gave the same type of addition product as was obtained with phosgene. Both adducts were dehydrohalogenated to the corresponding unsaturated ketones by heating with diethylaniline.

$$2C_6H_5CH{=}CH_2 + CH_2(COCl)_2 \xrightarrow[\text{CS}_2]{\text{SnCl}_4}$$

$$C_6H_5CHClCH_2COCH_2COCH_2CHClC_6H_5$$
(not isolated)

$$\xrightarrow[\text{180°C.}]{C_6H_5N(C_2H_5)_2} C_6H_5CH{=}CHCOCH_2COCH{=}CHC_6H_5$$
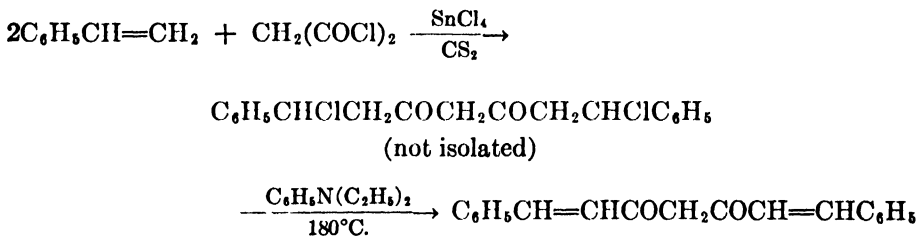
With such higher acid chlorides as stearoyl (89 per cent yield), lauroyl, oleoyl, linoleoyl, and linolenoyl in the presence of aluminum chloride, the nucleus was acylated without affecting the vinyl group (591, 592).

In the presence of mercuric chloride methyl α-chlorobenzyl ether added to styrene, but the structure of the product was not determined (715).

3,5-Dimethyl-2-hydroxystyrene reacted with chloroacetic acid in the presence of sodium hydroxide to give a product of undetermined structure (6).
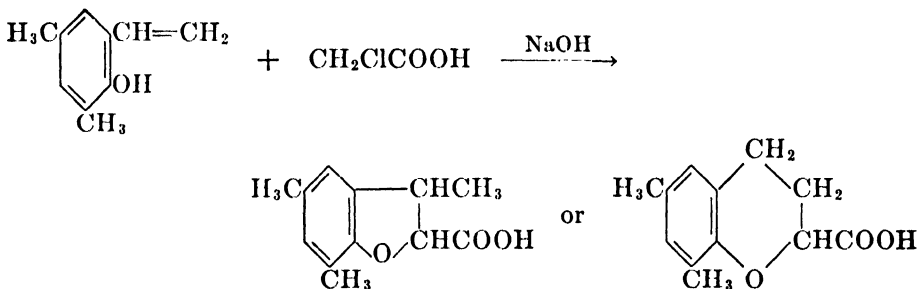
The reactions of α-methoxystyrene with acid chlorides and other halogen compounds have been discussed in connection with the chemistry of α-alkoxystyrenes.

When a carbon tetrachloride solution of styrene and carbon tetrabromide was irradiated with white light, a nearly quantitative yield of 1,1,1,3-tetrabromo-3-phenylpropane was obtained (370).

$$C_6H_5CH{=}CH_2 + CBr_4 \xrightarrow[\text{CCl}_4]{\text{light}} C_6H_5CHBrCH_2CBr_3$$
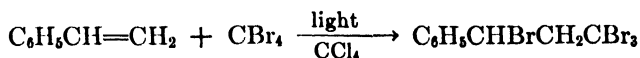
Styrene added bromotrichloromethane under similar conditions (369a).

At 295–305°C. and 33 atm. pressure in the presence of a zinc–copper–chromium oxide catalyst styrene reacted with carbon dioxide to give 0.28 per cent of cinnamic acid (388).

XV. REACTIONS WITH ALDEHYDES

Prins (573, 574, 575, 576) first condensed styrene with formaldehyde by means of a sulfuric acid catalyst in glacial acetic acid solution. The products were 40 per cent of 1-phenyltrimethylene glycol diacetate and some 4-phenyl-1,3-dioxane. Prins and subsequent workers (514) formulated these compounds incorrectly as derivatives of 2-phenyltrimethylene glycol. It was finally shown that the products

$$C_6H_5CH{=}CH_2 \; + \; HCHO \; + \; CH_3COOH \xrightarrow{\;H_2SO_4\;}$$

$$\underset{\displaystyle OCOCH_3}{C_6H_5CHCH_2CH_2OCOCH_3} \; + \; \underset{\displaystyle OCH_2O}{C_6H_5CHCH_2CH_2}$$
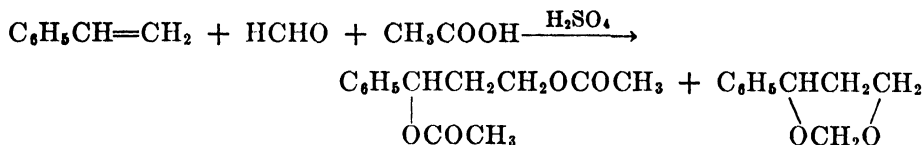
were really derivatives of 1-phenyltrimethylene glycol (230, 231), and the yields were raised to 48 per cent for the glycol diacetate and 30 per cent for the dioxane. The proof of structure consisted in preparing the dibenzoate of the glycol and

TABLE 42

Styrene and aldehydes

ALDEHYDE USED	R	R′	STY-RENE RECOV-ERED	$C_6H_5CH{=}CHCH{=}CRR'$	$\underset{\displaystyle CHRR'}{\overset{\displaystyle C_6H_5CHCH_2CHCHRR'}{O{-}CH{-}O}}$	GLYCOL MONO-ACETATE
			per cent	*per cent*	*per cent*	*per cent*
Acetaldehyde.....	H	H	5	32	18	12 (di)
Propionaldehyde .	H	CH₃	18	8	10	26
n-Butyraldehyde .	H	C₂H₅	23	14	0	39
Isobutyraldehyde.	CH₃	CH₃	14	23	13	13

showing it to be identical with that of the glycol obtained by the reduction of methylolacetophenone.

With higher aldehydes the products were the dioxane, the substituted trimethylene glycol monoacetate (with acetaldehyde mostly the diacetate), and the substituted phenylbutadiene corresponding to the loss of two moles of water from the glycol (190). These products are summarized in table 42.

In the presence of hydrochloric acid styrene reacted with formaldehyde to give only 4-phenyl-1,3-dioxane (198). Styrene polymerized when an aldehyde condensation was attempted in the presence of light or peroxides (369a).

XVI. ADDITION REACTIONS

When the vapors of styrene and ethylene or acetylene were passed through a hot tube, benzene and naphthalene were produced (75, 79). Similarly from styrene and benzene, anthracene and some naphthalene were obtained. With tetrafluoroethylene styrene yielded 85 per cent of 1-phenyl-2,2,3,3-tetrafluorocyclobutane (141a).

Styrene added diphenylketene to give a 93 per cent yield (706) of a triphenyl-cyclobutanone (65, 705).

$$C_6H_5CH{=}CH_2 + (C_6H_5)_2C{=}CO \longrightarrow \begin{array}{c} C_6H_5CH{-}CH_2 \\ | \quad\quad | \\ (C_6H_5)_2C{-}\!-\!CO \end{array}$$

The reaction was postulated originally as proceeding in the reverse fashion (706), but subsequent work showed the phenyl groups to be on adjacent carbon atoms (705). The addition of diphenylketene also was observed in the case of the following styrenes: p-methyl- (81 per cent yield), p-chloro- (82 per cent yield), and p-methoxy- (84 per cent yield) (706).

When exposed to sunlight in thiophene-free benzene solution, styrene added phenanthrenequinone (659, 660).

$$\text{phenanthrenequinone} + C_6H_5CH{=}CH_2 \longrightarrow \text{product}$$

Styrene reacted with methyl acetylenedicarboxylate to give a compound of unknown structure (9). The product with ethyl azodicarboxylate was formulated as a ring compound containing four nitrogen atoms (348).

$$C_6H_5CH{=}CH_2 + 2C_2H_5OCON{=}NCOOC_2H_5 \longrightarrow$$

$$\begin{array}{c} NCOOC_2H_5 \\ C_6H_5CH \quad\quad NCOOC_2H_5 \\ | \quad\quad\quad\quad | \\ H_2C \quad\quad\quad NCOOC_2H_5 \\ NCOOC_2H_5 \end{array}$$

With the methyl ester the product, obtained in quantitative yield, was formulated as involving condensation with the benzene ring (162).

$$C_6H_5CH{=}CH_2 + CH_3OCON{=}NCOOCH_3 \longrightarrow$$

$$\xrightarrow{\quad CH_3OCON{=}NCOOCH_3 \quad}$$

$$CH_3OCONNHCOOCH_3$$

Styrene readily serves as the olefinic component in the Diels–Alder reaction. Such diolefins were added as butadiene (33 per cent yield), 2,3-dimethylbutadiene (38 per cent yield), cyclopentadiene (10 per cent yield) (10), 2,5-diphenylisobenzofuran, and 2,5-diphenyliso(3′,4′-dimethyl)benzofuran (16). In the case of cyclopentadiene 12 per cent of the product containing two moles of cyclopentadiene also was obtained.

$$C_6H_5CH{=}CH_2 \; + \; \begin{array}{c} HC\text{----}CH \\ \| \quad \| \\ HC \quad CH \\ \diagdown \diagup \\ CH_2 \end{array} \rightarrow$$
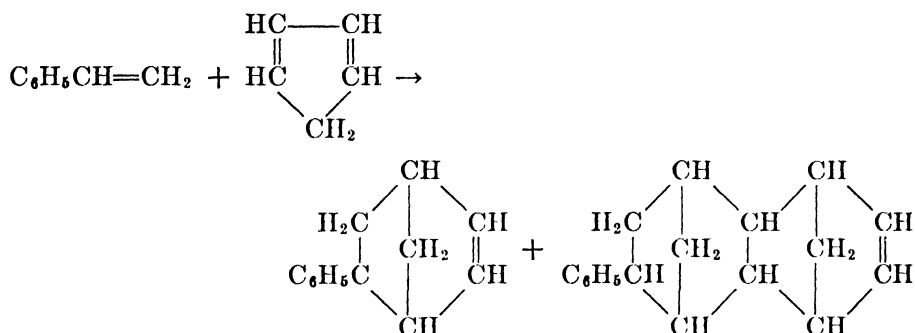
With tetraphenylcyclopentadienone (1a) and 2,5-diphenyl-3,4-bis(3′,4′-methylenedioxy)phenylcyclopentadienone (27) the carbonyl bridge was lost.
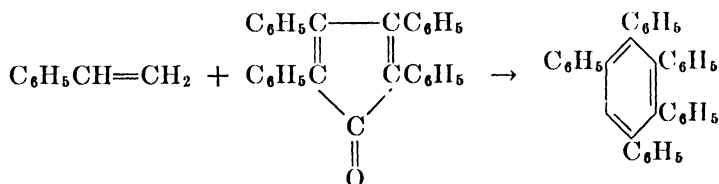
Styrene did not react with quinone (751).

The diene addition reactions of β-nitrostyrene are summarized in table 43.

XVII. CONDENSATION REACTIONS

In the presence of acid catalysts styrene reacts with aromatic compounds, particularly with those possessing reactive nuclei, to give products of the type $C_6H_5CHRCH_3$, where R is the aryl nucleus in question. These reactions are summarized in table 44.

2,4-Dihydroxystyrene reacted with resorcinol to give 10 per cent of an adduct which also had lost water (223).
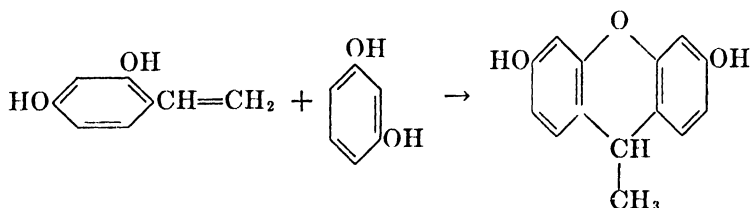
The reactions of α-methoxystyrene with various hydrocarbons have been discussed in connection with α-alkoxystyrenes.

XVIII. REACTIONS NOT INVOLVING THE VINYL GROUP

The preceding seventeen sections have been devoted to reactions occurring at the double bonds in the various styrenes considered. Section XVIII is concerned

TABLE 43

β-Nitrostyrene and dienes

DIENE ADDED	YIELD	REFERENCE
	per cent	
Butadiene..............	70	(16)
Isoprene....	58	(16)
2,3-Dimethylbutadiene	82	(15, 16)
2,3-Diphenylbutadiene........	9	(15, 16)
1,4-Diphenylbutadiene...............	80	(16)
Cyclopentadiene.	95	(15, 16)
Cyclohexadiene.......	20–25	(15, 16)
Phellandrene......................	45	(15, 16)
1,1'-Bicyclohexenyl.....	95	(69)
Methyleneanthrone*......	3	(15, 16)
2,5-Diphenylisobenzofuran................	Quantitative	(16)
2,5-Diphenyliso(3',4'-dimethyl)benzofuran ..	Quantitative	(16)
Furan................................	0	(16)
Sylvan......	0	(16)
2,5-Dimethylfuran.....................	0	(16)

* In this reaction the principal product (25 per cent yield) was that in which nitrous acid had been lost:
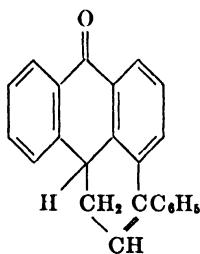
Similarly with tetraphenylcyclopentadienone only pentaphenylbenzene was isolated (15, 16).

with reactions of other parts of the molecule during the course of which the double bond remains intact.

Phenolic hydroxyl groups undergo a variety of reactions which do not affect vinyl groups in the same molecule. The following styrenes have been acetylated by means of acetic anhydride: 3-methoxy-4-hydroxy- (249), 2,4-dihydroxy- (223), 2-hydroxy-3,5-dibromo- (248), 2-hydroxy-β,3,5-tribromo- (248), 4-hy-

TABLE 44

Condensation reactions of styrene

AROMATIC COMPOUND	CATALYST	TEMPERATURE	PRODUCT	YIELD	REFERENCE
		°C.		per cent	
Benzene......... {	$AlCl_3$	25	$(C_6H_5)_2CHCH_3$	5	(533)
	93% H_2SO_4	30–35	$(C_6H_5)_2CHCH_3$	25	(702)
Toluene........ {	H_2SO_4		Structure not given	46	(417, 418)
	93% H_2SO_4		Structure not given		(702)
o-Xylene........ {	H_2SO_4		$C_6H_5CH(CH_3)$ with H_3C, CH_3, CH_3 substituents	66	(417, 418)
	93% H_2SO_4				(702)
m-Xylene....... {	H_2SO_4		$C_6H_5CH(CH_3)$ with H_3C, H_3C, CH_3 substituents	63	(417, 418)
	93% H_2SO_4				(702)
p-Xylene....... {	H_2SO_4		$C_6H_5CH(CH_3)$ with H_3C, H_3C, CH_3 substituents		(417, 418)
	93% H_2SO_4				(702)
Pseudocumene....	H_2SO_4		Structure not given	65	(417, 418)
Xylene...........	H_2SO_4		Structure not given		(416)
Naphthalene.......	Cerium metaphosphate	380	Reddish oil		(323)
Tetralin.... {	H_2SO_4		$C_6H_5CH(CH_3)$ fused bicyclic structure		(114)
	93% H_2SO_4		Structure not given		(702)
Decalin..	93% H_2SO_4	30–35	$C_6H_5CH(CH_3)$ decalin structure	52	(702)
Hydrindene.......	93% H_2SO_4		Structure not given		(702)
Anisole	Bleaching earth		Resin and oil		(326)
Glycol monophenyl ether	Bleaching earth		Resin and oil		(326)
Diphenyl ether .	Retrol	270	Monocondensation product Polycondensation product	26	(685)

TABLE 44—*Continued*

AROMATIC COMPOUND	CATALYST	TEMPER-ATURE	PRODUCT	YIELD	REFERENCE
		°C.		per cent	
o-Phenoxybi-phenyl	Retrol	270	Monocondensation product	26	(685)
			Polycondensation product		
	H₂SO₄		Mono-, di-, and poly-condensation products		(769)
	Bleaching earth	90	Resin and oil		(326)
Phenol	H₂SO₄, CH₃COOH		H_3C	40	(396, 397)
	HCl		C_6H_5CH⟨C₆H₃⟩OH	65	(544)
	HI				(711)
o-Cresol.........	HI		H_3C		(397)
			C_6H_5CH⟨C₆H₂⟩OH with CH₃		
m-Cresol.........	HI		H_3C	32	(397)
			C_6H_5CH⟨C₆H₂⟩OH with H₃C		
	Bleaching earth		Resin and oil		(326)
p-Cresol.........	H₂SO₄, CH₃COOH		None		(397)
α-Naphthol.......	H₂SO₄, CH₃COOH		None		(397)
β-Naphthol	H₂SO₄, CH₃COOH		H_3C C_6H_5CH⟨naphthyl⟩ HO		(397)
Resorcinol.......	H₂SO₄, CH₃COOH		H_3C HO		(396)
	HClO₄, CH₃COOH		C_6H_5CH⟨C₆H₃⟩OH	51	(653)

TABLE 44—*Concluded*

AROMATIC COMPOUND	CATALYST	TEMPER-ATURE	PRODUCT	YIELD	REFERENCE
		°C.		per cent	
Aniline..........	Aniline hydro-chloride	200–240		8	(299)
				18	
				3	
p-Toluidine.......	p-Toluidine hydrochloride	260–270		14	(299)
				3	
2,4-Xylidine......	2,4-Xylidine hydrochloride	255–290		4	(299)

droxy-2,3,5-tribromo- (816), 4-hydroxy-β,2,3,5-tetrabromo- (816), and 4-hy-droxy-β,2,3,5,6-pentabromo- (816). 3-Methoxy-4-hydroxystyrene also yielded a carbonate on treatment with phosgene (249, 610), a benzoate by the Schotten–Baumann procedure (249, 610), a p-nitrobenzoate (610), and a 3,5-dinitro-benzoate (561). m-Hydroxystyrene was benzoylated by the Schotten–Baumann procedure (404).

Phenoxyacetic acids have been prepared from the following substituted sty-renes by treatment with chloro- or bromo-acetic acids in the presence of alkali: o-hydroxy- (686), 2-hydroxy-5-methyl- (6), and 3-methoxy-4-hydroxy- (249, 610).

$$CH_2{=}CH\langle\;\rangle OH + CH_2ClCOOH \xrightarrow{KOH}$$
$$\qquad\qquad OCH_3$$

$$CH_2{=}CH\langle\;\rangle OCH_2COOH$$
$$\qquad\qquad\qquad OCH_3$$
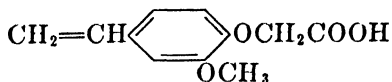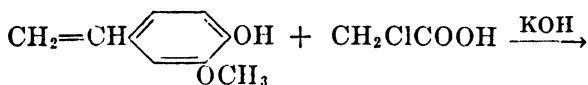
Treatment of 3-methoxy-4-hydroxystyrene with methyl iodide and sodium hydroxide gave the methyl ether (249, 610).

The phenylurethan of 3-hydroxy-4-ethoxystyrene has been prepared (359). Hydrolysis of p-vinylbenzyl acetate with alcoholic potassium hydroxide yielded 38 per cent of p-vinylbenzyl alcohol (197a).

The o-, m-, and p-aminostyrenes (404, 557) as well as o-amino-β-chloro- (404, 405, 453, 504) and o-amino-β-bromo-styrenes (404) have all been prepared by reducing the corresponding nitrostyrene with stannous chloride and hydrochloric acid. m-Nitrostyrene was reduced to 3,3'-divinylazobenzene in 69 per cent yield by means of sodium stannite and the latter compound converted to 2,2'-divinylbenzidine in 25 per cent yield by means of stannous chloride and hydrochloric acid followed by concentrated hydrochloric acid (404).
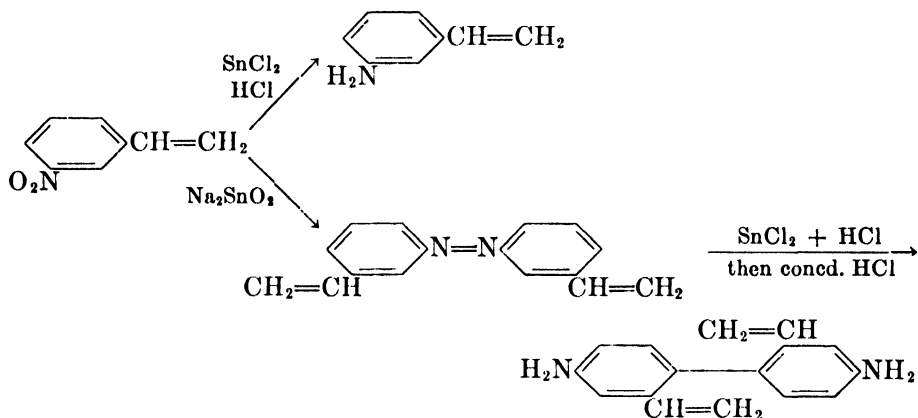
In a more recent investigation (778c) only polymer could be obtained when m-nitrostyrene was treated with zinc and hydrochloric acid or with stannous chloride. With sodium methoxide or zinc and ammonium chloride m-nitrostyrene yielded 3,3'-divinylazoxybenzene. Reduction of m-nitrostyrene with zinc and alcoholic sodium hydroxide gave 3,3'-divinylhydrazobenzene. This latter compound was oxidized to 3,3'-divinylazobenzene by means of alcoholic ferric chloride, sodium hypobromite, or air and sodium hydroxide. With concentrated hydrochloric acid in ether 3,3'-divinylhydrazobenzene yielded 30 per cent of 2,2'-divinylbenzidine.

Acetamides have been prepared from the following styrenes by treatment with acetic anhydride: o-amino- (404), m-amino- (75 per cent yield) (404), p-amino- (404), and o-amino-β-chloro- (404, 405). Benzamides have been prepared from the following styrenes by treatment with benzoyl chloride in the presence of alkali: m-amino- (404, 758) and p-amino- (404). m-Aminostyrene also reacted with potassium cyanate to give a substituted urea (404).
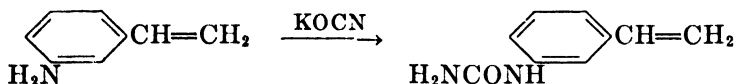
Treatment of a mixture of m- and p-aminostyrenes with phosgene in toluene yielded 71 per cent of the corresponding isocyanates (419a). 2-Methyl-5-vinylphenylisocyanate was prepared by the same method in 31 per cent yield.
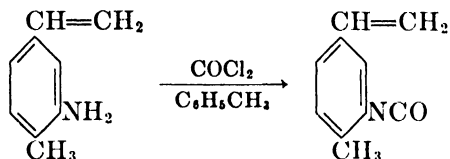
While the diazotization of o-aminostyrene gave impure o-hydroxystyrene (557), a 39 per cent yield of o-hydroxy-β-chlorostyrene was obtained from the diazotization of o-amino-β-chlorostyrene (404, 405). The diazotization of p-aminostyrene gave only tar (71, 404, 557). On the other hand m-aminostyrene gave a stable diazonium salt (404). Treatment with steam gave a 69 per cent yield of m-hydroxystyrene, with cuprous cyanide m-cyanostyrene, and with aniline m-vinyldiazoaminobenzene. The m-cyanostyrene was hydrolyzed to m-carboxystyrene by boiling with alcoholic potassium hydroxide.
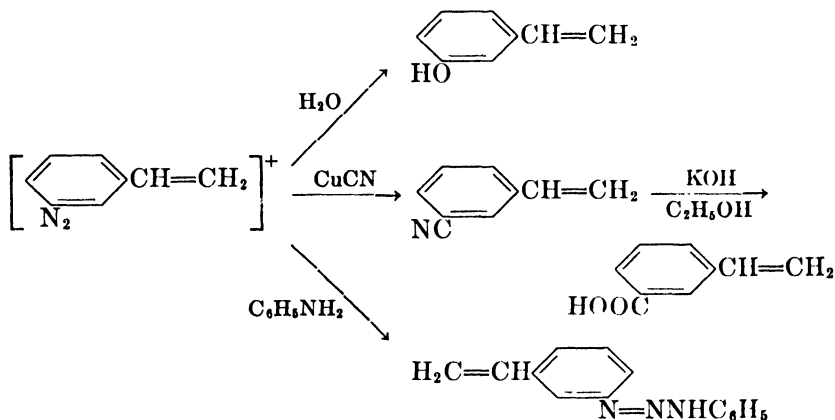
2,2'-Divinylbenzidine also has been diazotized and coupled.

Both o-dimethylaminomethyl- (109, 188) and o-(β-dimethylaminoethyl)-styrenes (116) readily add methyl iodide to give quaternary salts. The iodide from dimethylaminomethylstyrene was converted to the chloride with silver chloride and this latter compound was reduced to o-methylstyrene by means of sodium amalgam and water (188).
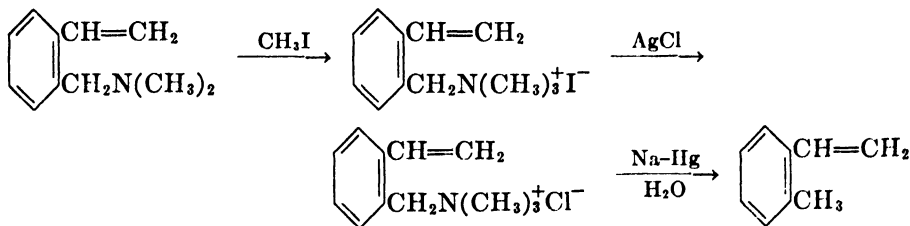
Treatment of *o*-dimethylaminomethyl- (50 per cent yield) (110), *o*-piperidino-methyl- (109), and *o*-pyrrolidinomethyl-styrenes (109) with cyanogen bromide gave *o*-bromomethylstyrene and the corresponding cyanamide.
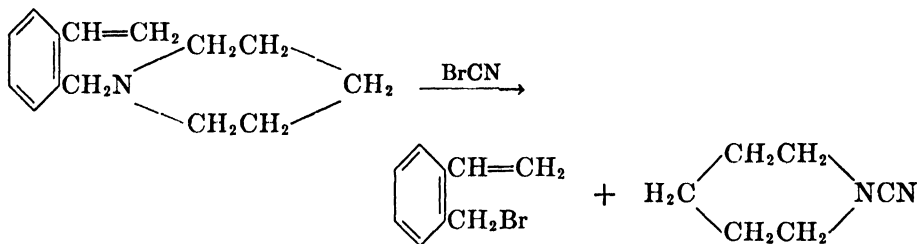
m-Cyano-β-nitrostyrene was converted to the imino methyl ether in 28 per cent yield by means of hydrogen chloride and methanol in ether (682). This compound was hydrolyzed with water to give a small amount of *m*-carboxy-β-nitro-styrene.
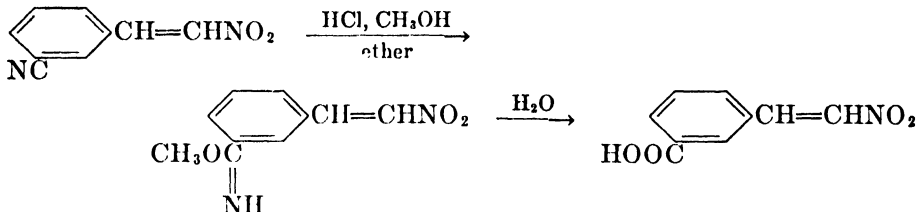
p-Vinylbenzaldehyde formed a phenylhydrazone and was oxidized by means of silver oxide to a 75 per cent yield of *p*-vinylbenzoic acid (778a).

o-Vinylphenylarsonic acid was converted to *o*-vinylphenyldichloroarsine by treatment with sulfur dioxide and hydrogen chloride (151, 152).
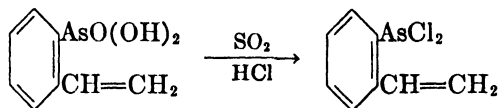
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THE PREPARATION OF SUBSTITUTED STYRENES BY METHODS NOT INVOLVING HYDROCARBON CRACKING

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CONTENTS

I. INTRODUCTION

This review summarizes the methods for preparing nuclear-substituted styrenes and β-nitrostyrenes by those methods which do not involve the cracking of hydrocarbons. In this sense it is a supplement to "The Reactions of Monomeric Styrenes" (43), which reviews the preparation of styrenes substituted in the side chain and the reactions of substituted styrenes. The literature and types of compounds covered are identical with those in the former review.

II. DEHYDRATION OF ALCOHOLS

This method for preparing substituted styrenes has received particular attention during the last few years in connection with the synthetic rubber program of the United States Government. α-Phenethyl alcohols can be obtained easily by the Grignard reaction from the corresponding aryl bromide or iodide or the corresponding aromatic aldehyde. An equally convenient preparation is the reduction of the corresponding acetophenone.

$$ArMgBr + CH_3CHO \rightarrow ArCHOHCH_3$$

$$ArCHO + CH_3MgI \rightarrow ArCHOHCH_3$$

$$ArCOCH_3 \xrightarrow{(H)} ArCHOHCH_3$$
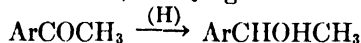
This method is limited only by the availability of these intermediates and obviously is capable of very extensive application.

The earliest method of dehydration, and one that has been used occasionally in recent years, was simply to distil the alcohol slowly. As a matter of fact Bottcher (14) observed that when he decomposed the adduct from piperonal and methylmagnesium iodide with dilute sulfuric acid he obtained the olefin directly,

---

TABLE 1

Dehydration of α-phenethyl alcohols by distillation

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
p-Isopropyl...........................		(94)
p-Methoxy......................... {	Good	(118) (199)
3,4-Dimethoxy..................... {		(9) (57)
3,4-Methylenedioxy................ {	82	(141) (14) (93) (116) (87)
p-Dimethylamino................... {	45 30 0	(125) (204) (180)

whereas with aqueous ammonium chloride the carbinol was obtained in 90 per cent yield.
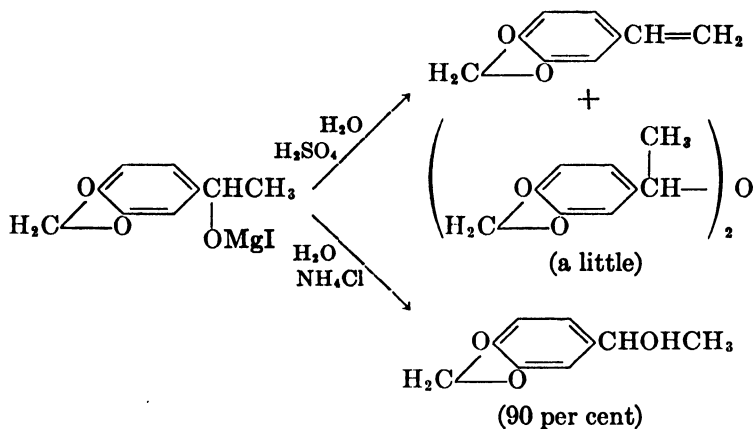
Mannich and Jacobsohn (118) obtained a good yield of p-methoxystyrene when they decomposed the adduct from anisaldehyde and methylmagnesium iodide with dilute sulfuric acid. In table 1 are summarized the preparations of substituted styrenes by the distillation of the corresponding α-phenethyl alcohol.

$$ArCHOHCH_3 \xrightarrow{\text{distil}} ArCH{=}CH_2 + H_2O$$
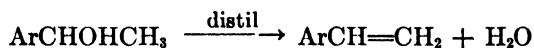
2,3-Dimethoxystyrene has been prepared by steam distilling the corresponding α-phenethyl alcohol (77).

When p-methoxystyrene was obtained directly from the Grignard reaction, some p-methoxy-α-phenethyl alcohol also was isolated, as well as some p-methoxy-α-phenethyl ether (199). In the case of 3,4-methylenedioxystyrene, besides 3,4-methylenedioxy-α-phenethyl alcohol (116), both 3,4-methylenedioxy-α-phenethyl ether (14) and 3,4-methylenedioxyacetophenone (116) were isolated.

When m-benzoxybenzaldehyde was treated with methylmagnesium iodide and the product hydrolyzed with aqueous potassium hydroxide, m-hydroxystyrene was produced (77).

$$C_6H_5COO\text{-}C_6H_4\text{-}CHO + CH_3MgI \xrightarrow[\text{H}_2\text{O} + \text{KOH}]{\text{then}} HO\text{-}C_6H_4\text{-}CH=CH_2$$
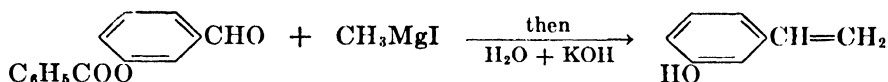
TABLE 2

Dehydration of α-phenethyl alcohols with phosphorus pentoxide

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
m-*tert*-Butyl	40	(120)
m-Bromo	51	(24)
p-Bromo	40–44	(159)
m-Trifluoromethyl	54	(125)
m-Nitro	25	(125)

Acetaldehyde reacted with p-hexylphenylmagnesium bromide to give 18 per cent of p-hexylstyrene, some p-hexylacetophenone, 2–3 per cent of p-hexylbiphenyl, and polymeric products (120).

$$C_6H_{13}\text{-}C_6H_4\text{-}MgBr + CH_3CHO \rightarrow C_6H_{13}\text{-}C_6H_4\text{-}CH=CH_2 +$$

(18 per cent)

$$C_6H_{13}\text{-}C_6H_4\text{-}COCH_3 + C_6H_{13}\text{-}C_6H_4\text{-}C_6H_4\text{-}C_6H_{13} + \text{polymer}$$

(2–3 per cent)
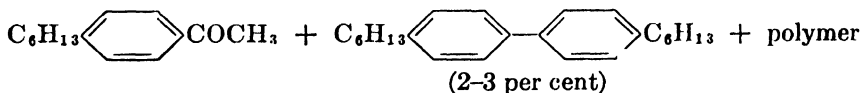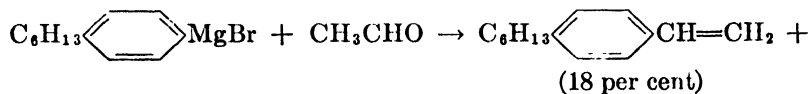
Reduction of 2,5-diethylacetophenone with sodium and alcohol yielded 2,5-diethylstyrene (94).

$$C_2H_5\text{-}C_6H_3(C_2H_5)\text{-}COCH_3 \xrightarrow{\text{Na}}_{\text{C}_2\text{H}_5\text{OH}} C_2H_5\text{-}C_6H_3(C_2H_5)\text{-}CH=CH_2$$
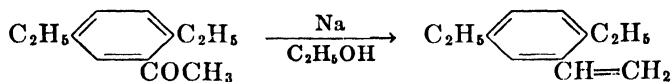
The electrolysis of ether solutions of p-methylphenylmagnesium bromide and of p-chlorophenylmagnesium bromide yielded the corresponding styrenes (51).

Since the direct distillation of α-phenethyl alcohols usually is not a particularly effective method of dehydration, a variety of dehydrating agents have been employed. In the liquid phase phosphorus pentoxide in boiling benzene has proven to be reasonably useful. In table 2 are listed the substituted styrenes

$$ArCHOHCH_3 \xrightarrow[\text{C}_6\text{H}_6]{\text{P}_2\text{O}_5} ArCH=CH_2$$
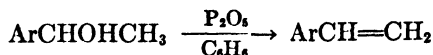
which have been prepared in this manner.

Treatment of o-methoxymethyleneoxy-α-phenethyl alcohol with alcoholic sulfuric acid yielded o-vinylphenol (76).
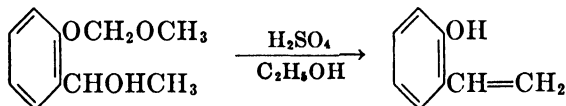
Treatment of 2,4,5-trimethyl-α-phenethyl alcohol with phosphoric acid yielded only polymer (92).

A great many substituted styrenes have been prepared by distilling the corresponding α-phenethyl alcohol from a dehydrating agent. Thus, o-chlorostyrene was obtained in 80–94 per cent yields in this way from o-chloro-α-phenethyl alcohol (215). 2,5-Dimethyl-3,6-dimethoxystyrene was obtained similarly by distilling the corresponding α-phenethyl alcohol from a drop of sulfuric acid (196).
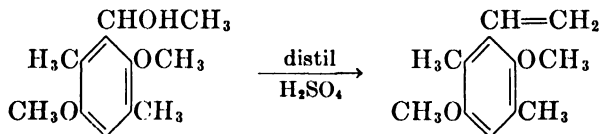
The following styrenes were obtained by distilling the corresponding α-phenethyl alcohols from phosphorus pentoxide: 2,4,6-trimethyl- (92), m-trifluoromethyl- (79 per cent yield) (7), p-fluoro-m-trifluoromethyl- (70 per cent yield) (7), and o-bromo-p-trifluoromethyl- (7).

Probably the most widely used preparation of substituted styrenes is the distillation of the corresponding α-phenethyl alcohol from sodium bisulfate, potassium bisulfate, or potassium pyrosulfate. This operation usually is conducted at

$$\text{ArCHOHCH}_3 \xrightarrow{\text{KHSO}_4} \text{ArCH}=\text{CH}_2$$

reduced pressure and at temperatures of 175–230°C. In table 3 are listed the substituted styrenes which have been prepared in this way.

Another widely used method for dehydrating α-phenethyl alcohols is to pass their vapors over activated alumina at 250–450°C. (usually 300–350°C.), generally at reduced pressures.

$$\text{ArCHOHCH}_3 \xrightarrow[300-350°C.]{\text{Al}_2\text{O}_3} \text{ArCH}=\text{CH}_2 + \text{H}_2\text{O}$$
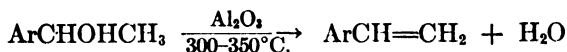
This method suffers from the disadvantage that some disproportionation may occur to give the corresponding ethylbenzene and acetophenone.

$$\text{ArCHOHCH}_3 \xrightarrow[300-350°C.]{\text{Al}_2\text{O}_3} \text{ArCH}_2\text{CH}_3 + \text{ArCOCH}_3$$
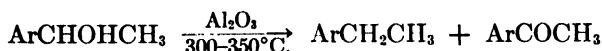
Acetophenone has been isolated from such a pyrolysis of methylphenylcarbinol itself (79). When p-benzyl- (121), o-methoxy- (121), and p-phenoxy-styrenes

(57) were prepared in this way, they were all contaminated with some of the corresponding ethylbenzene. In the case of o-methoxystyrene (121), some o-ethylphenol also was isolated, presumably from demethylation of the o-ethylanisole. Pyrolysis of (m-methylaminophenyl)methylcarbinol gave as the sole product 48 per cent of m-(methylamino)ethylbenzene (122). In table 4 are listed those sub-

TABLE 3

Dehydration of α-phenethyl alcohols with bisulfates

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE	SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent			*per cent*	
o-Methyl...................		(41)		86	(23)
m-Methyl..................	50	(125)	p-Chloro.................	60	(127)
				47	(203)
	72	(206a)			
p-Methyl................		(41)	2,3-Dichloro.............	44	(124)
		(66)	2,4-Dichloro.............	33	(124)
		(203)	2,5-Dichloro.............	37	(23)
			2,6-Dichloro.............	32	(124)
2,4-Dimethyl...............	71	(126)			
2,5-Dimethyl...............	88	(126)	3,4-Dichloro.............	83	(23)
3,4-Dimethyl...............	80	(126)		64	(124)
3,5-Dimethyl..............	87	(126)			
			3,5-Dichloro.............	43	(124)
p-Ethyl................	80	(66)	o-Bromo.................		(189)
	72	(206a)	m-Bromo................	Low	(24)
p-n-Butyl..................	70	(206a)	p-Bromo................		(189)
m-sec-Butyl................	61	(120)			(229)
m-tert-Butyl..............	61	(120)			
p-n-Heptyl..............	69	(206a)	p-Iodo..............	60	(204)
p-(2-Ethylhexyl)...........	30	(206a)	o-Methoxy.............		(189)
o-Fluoro................	76	(23)			
m-Fluoro..................	80	(23)	p-Methoxy.............		(189)
					(203)
p-Fluoro............	81	(23)			
	62	(7)	2,6-Dimethoxy............	60	(186)
			p-Acetoxy.............	45	(45)
Chloro...................		(181)	p-Carbomethoxy.........	49	(44)
o-Chloro	70	(23)	d-p-(sec-Butoxymethylene).	47	(123)
			o-Amino..........		(189)
m-Chloro.................	83	(23)	p-Amino.............		(189)
	23	(127)			

stituted styrenes which have been prepared by dehydration of the corresponding carbinols over activated alumina.

When alumina on pumice was used for the preparation of p-ethylstyrene at 300°C., some alcohol was recovered and some p-ethyl-α-phenethyl ether was obtained (80). When the vapors of p-carbethoxy-α-phenethyl alcohol together

with steam were passed over activated alumina at 300–350°C., 8 per cent of p-vinylbenzoic acid was isolated along with 35 per cent of its polymer (44).

$$CH_3CHOH\langle\underset{}{\bigcirc}\rangle COOC_2H_5 + H_2O \xrightarrow[300-350°C.]{Al_2O_3}$$

$$CH_2{=}CH\langle\underset{}{\bigcirc}\rangle COOH$$
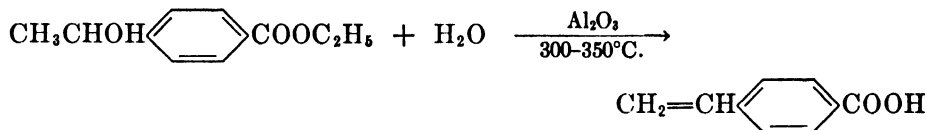
β-Phenethyl alcohols also are dehydrated very smoothly and in general give purer products than do the α-isomers (57, 121). This operation uniformly has been effected by distilling the alcohol from solid potassium hydroxide with a pot temperature of about 200°C., usually in a copper vessel. These alcohols

TABLE 4

Dehydration of α-phenethyl alcohols over activated alumina

SUBSTITUTED STYRENE OBTAINED	YIELD	REFER-ENCE	SUBSTITUTED STYRENE OBTAINED	YIELD	REFER-ENCE
	per cent			*per cent*	
p-Methyl	83	(134)	3,5-Dichloro		(133)
m-Trifluoromethyl	79	(171)	2,3,4,5,6-Pentachloro	61	(178)
m-Ethyl	93	(134)	o-Methoxy		(121)
p-Ethyl	83	(134)	p-Methoxy	65	(134)
3,5-Diethyl	83	(134)	p-Ethoxy	69	(134)
p-tert-Butyl	76	(134)			
p-Hexyl	87	(134)			
p-Benzyl	83	(121)	p-Phenoxy	72	(134) (57)
p-Fluoro	89	(171)			
m-Chloro	84	(47)			
2,3-Dichloro		(133)	p-Cyano	71	(134)
2,4-Dichloro		(133)	p-Amino	20	(134)
2,5-Dichloro		(133)			
2,6-Dichloro		(133)	p-Vinyl	83	(134)
3,4-Dichloro	87	(134)		81	(73)

generally are prepared by treating the corresponding arylmagnesium halide with ethylene oxide.

$$ArMgX + H_2C{-}CH_2 \xrightarrow{\quad} ArCH_2CH_2OH$$
$$\underset{O}{\diagdown\diagup}$$
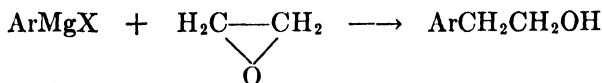
In table 5 are listed the substituted styrenes which have been prepared from alcohols in this manner.

$$ArCH_2CH_2OH \xrightarrow[200°C.]{KOH} ArCH{=}CH_2 + H_2O$$
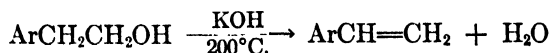
The dehydration of a β-phenethyl alcohol possibly is involved in the reaction of phenol with ethylene oxide in the presence of concentrated sulfuric acid to give 65 per cent of o-vinylphenol (195).

$$C_6H_5OH \; + \; H_2C\!\!-\!\!CH_2 \xrightarrow[\text{H}_2\text{SO}_4]{\text{concd.}}$$

(65 per cent)
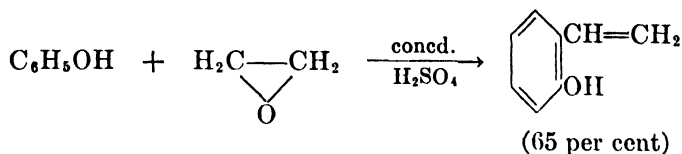
Treatment of β-hydroxyethyl phenyl ether with concentrated sulfuric acid gave the same product.

III. PYROLYSIS OF ESTERS AND ETHERS

Occasionally the pyrolysis of an ether or ester has proven to be more useful for the preparation of a substituted styrene than the dehydration of the corresponding α-phenethyl alcohol. The following styrenes have been prepared by

TABLE 5

Dehydration of β-phenethyl alcohols with potassium hydroxide

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
o-Methyl		(188)
m-Methyl		(188)
p-Methyl	Good	(128)
p-Methyl		(179)
p-Methyl		(188)
2,4-Dimethyl		(71)
p-Ethyl		(129)
Fluoro		(36)
p-Fluoro	23	(7)
(o + p)-Chloro		(139)
(o + p)-Bromo		(139)
m-Trifluoromethyl	72	(7)
o-Methoxy	69	(121)
m-Methoxy	69	(57)
p-Phenoxy	77	(57)

pyrolyzing the α phenethyl acetates in question over glass at 480–600°C.: 3,4-dichloro- (85 per cent yield) (124), p-acetoxy- (90 per cent yield) (2), and p-cyano-(76 per cent yield) (138). In the case of p-acetoxymethylene-α-phenethyl acetate a silica catalyst was used and steam was used as a carrier to prevent the tube from clogging (46). The yield was 72 per cent. Hydrolysis of this ester with alcoholic potassium hydroxide yielded 38 per cent of p-vinylbenzyl alcohol.

(72 per cent)
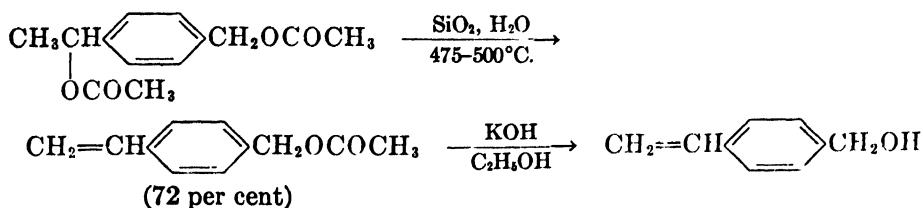
Pyrolysis of *p*-dimethylamino-α-phenethyl acetate was not effective for the preparation of *p*-dimethylaminostyrene (180).

In the case of 2,4,5-trimethyl-α-phenethyl acetate, boiling with potassium hydroxide in methanol yielded 2,4,5-trimethylstyrene (92). With 2,4,6-tri-

methyl-α-phenethyl acetate only the alcohol was obtained.
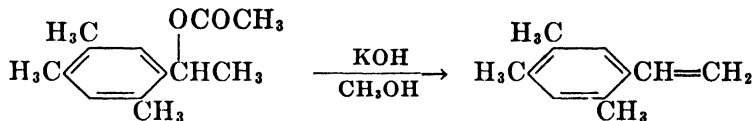
When vapors of *p*-phenoxy-α-phenethyl isopropyl ether were passed over alumina at 325–450°C., *p*-phenoxystyrene was obtained (57). Distillation was sufficient to convert 3,4-methylenedioxy-α-phenethyl ether to 3,4-methylenedioxystyrene (14). When the vapors of *o*-methoxy-α-phenethyl ether were passed over activated alumina at 310°C., a 75 per cent yield of *o*-methoxystyrene was obtained (121). At 550°C. in a stream of nitrogen 2-hydroxy-3,5-dimethylstyrene was obtained from 2,4,6,8-tetramethylbenzo-1,3-dioxane (1).
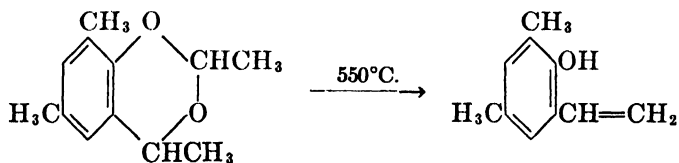
IV. DEHYDROHALOGENATION OF HALIDES

In many cases the dehydrohalogenation of α- or β-phenethyl halides has been used to prepare nuclear-substituted styrenes. The simplest procedure, which has been effective in a few instances, is to distil the halide in question. Thus, trichlorostyrene (114) and 2,3,4,5,6-pentachlorostyrene (86 per cent yield) (113) have been prepared by distilling the corresponding α-phenethyl chlorides three times and twice, respectively. When *o*-ethylphenol was treated with
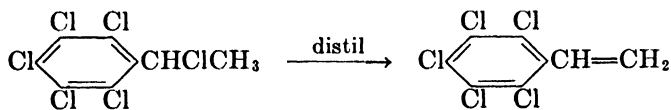
bromine and then distilled, a crude tribromo-*o*-hydroxystyrene was obtained (206). It was purified by treatment with alcoholic potassium hydroxide. Both *o*- (34) and *m*-vinyl-α-phenethyl bromides (33) have been prepared by distillation.
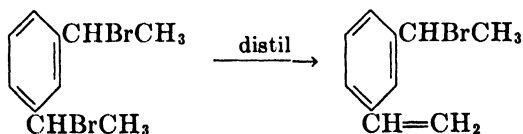
In table 6 are shown those substituted styrenes which have been prepared by treating a phenethyl halide with alcoholic potassium hydroxide.

$$\text{ArCHXCH}_3 \text{ or ArCH}_2\text{CH}_2\text{X} \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}} \text{ArCH=CH}_2$$

In the p-methylstyrene preparation some p-methyl-α-phenethyl ether also was isolated (184).

$$\text{H}_3\text{C}\langle\bigcirc\rangle\text{CHBrCH}_3 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KOH}}$$

$$\text{H}_3\text{C}\langle\bigcirc\rangle\text{CH=CH}_2 + \text{H}_3\text{C}\langle\bigcirc\rangle\underset{\overset{|}{\text{OC}_2\text{H}_5}}{\text{CHCH}_3}$$
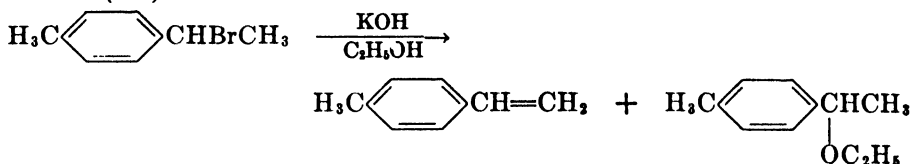
TABLE 6

Dehydrohalogenation of phenethyl halides with alcoholic potassium hydroxide

SUBSTITUTED STYRENE OBTAINED	HALIDE USED	YIELD	REFERENCE
		per cent	
p-Methyl...........................	α-Bromo	15	(184)
p-Chloro.............................	α-Chloro	Quantitative	(220a)
(o + p)-Bromo.......................	α-Bromo		(184)
2,3,4,5,6-Pentachloro................	α-Chloro	87	(113)
	α-Chloro	4	(178)
	β-Chloro	60	(178)
p-(N,N-Dimethylsulfonamido).........	β-Bromo	67	(84)

p-Fluorostyrene has been prepared in 72 per cent yield by heating the corresponding β-phenethyl bromide with potassium hydroxide at 220°C. (56).

$$\text{F}\langle\bigcirc\rangle\text{CH}_2\text{CH}_2\text{Br} \xrightarrow[220°\text{C.}]{\text{KOH}} \text{F}\langle\bigcirc\rangle\text{CH=CH}_2$$
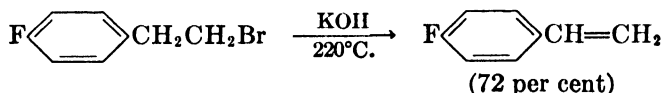
(72 per cent)

When anisole was treated with acetaldehyde and hydrochloric acid in the presence of zinc chloride and the product was treated with aqueous sodium carbonate, 80 per cent of di(p-methoxyphenyl)ethane and 12 per cent of p-methoxystyrene were obtained (161). The p-methoxystyrene undoubtedly was produced from p-methoxy-α-phenethyl chloride, a product of the initial condensation.

$$\text{C}_6\text{H}_5\text{OCH}_3 + \text{CH}_3\text{CHO} + \text{HCl} \xrightarrow{\text{ZnCl}_2}$$

$$\left[\text{CH}_3\text{O}\langle\bigcirc\rangle\text{CHClCH}_3\right] + \left[\text{CH}_3\text{O}\langle\bigcirc\rangle\right]_2\text{CHCH}_3$$

(80 per cent)

$$\xrightarrow[\text{Na}_2\text{CO}_3]{\text{aqueous}} \text{CH}_3\text{O}\langle\bigcirc\rangle\text{CH=CH}_2$$

(12 per cent)
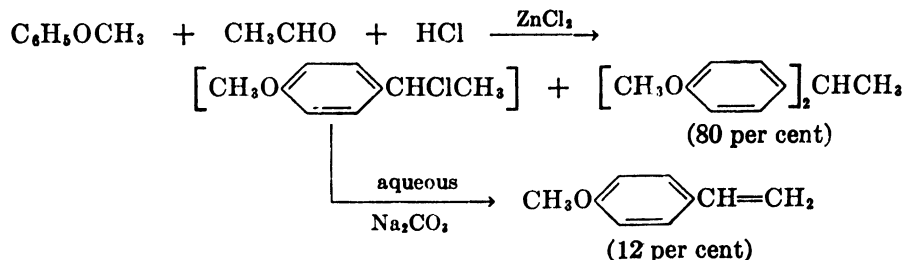
When p-methoxy-β-phenethyl bromide was condensed with phenyl isopropyl ketone by means of sodium amide in boiling benzene, considerable p-methoxystyrene was obtained as a by-product (26).

$$C_6H_5COCH(CH_3)_2 + CH_3O\!\!-\!\!\langle\ \rangle\!\!-\!\!CH_2CH_2Br \xrightarrow[C_6H_6]{NaNH_2}$$

$$CH_3O\!\!-\!\!\langle\ \rangle\!\!-\!\!CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}COC_6H_5 + CH_3O\!\!-\!\!\langle\ \rangle\!\!-\!\!CH\!\!=\!\!CH_2$$
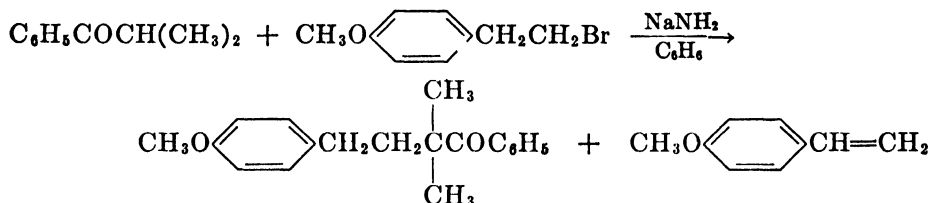
Chlorostyrene has been prepared by passing the vapors of the corresponding α-phenethyl chloride over a supported phosphoric acid–sodium phosphate catalyst (good yield) (82) or over mercurous chloride (92 per cent yield) (37) at 330–370°C. A mixture of dichlorostyrenes was obtained when mixed dichloro-α-chloroethylbenzenes were passed over silica gel in the presence of steam at 250–350°C. (50). When the vapors of α,m-dichloroethylbenzene together with steam were passed over calcium sulfate at 425–475°C., a 92.5 per cent yield of m-chlorostyrene was obtained (47). The o- and p-cyanostyrenes have been prepared in 57 per cent and 55 per cent yields, respectively, by passing the vapors of the corresponding α-chloroethylbenzenes over clay at 570–590°C. (220).

The most widely used method for dehydrochlorinating phenethyl halides is to pyrolyze a quaternary ammonium salt or hydroxide. In a great many cases no attempt has been made to isolate the quaternary salt, but instead the phenethyl halide is distilled with some tertiary amine. In table 7 are listed those substituted styrenes which have been prepared by distilling the corresponding α-phenethyl chloride with pyridine.

$$ArCHClCH_3 \xrightarrow{\text{pyridine}} ArCH\!\!=\!\!CH_2$$
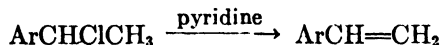
The α-phenethyl chlorides usually were prepared by treating the corresponding α-phenethyl alcohol with hydrogen chloride or, in the case of many of the alkoxy compounds, by chloroethylating the phenyl ether in question.

$$ArCHOHCH_3 \xrightarrow{HCl} ArCHClCH_3$$

$$C_6H_5OCH_3 + CH_3CHO + HCl \xrightarrow{ZnCl_2} CH_3O\!\!-\!\!\langle\ \rangle\!\!-\!\!CHClCH_3$$
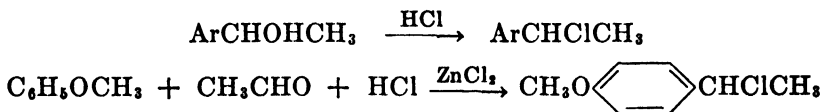
Treatment of p-dimethylamino-α-phenethyl alcohol with phosphorus pentachloride gave a mixture unsuitable for dehydrochlorination with pyridine (180).

2,4,6-Trimethylstyrene was obtained in low yield by heating 2,4,6-trimethyl-α-phenethyl chloride with aniline (92). Under the same conditions 2,4,5-trimethyl-α-phenethyl chloride yielded only polymer. p-Nitrostyrene was obtained in 85–91 per cent yield by heating p-nitro-β-phenethyl bromide with triethanolamine (204).

$$O_2N\!\!-\!\!\langle\ \rangle\!\!-\!\!CH_2CH_2Br \xrightarrow{(HOCH_2CH_2)_3N} O_2N\!\!-\!\!\langle\ \rangle\!\!-\!\!CH\!\!=\!\!CH_2$$
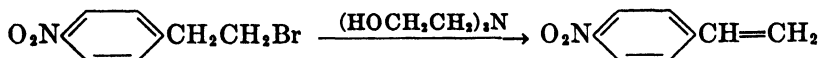
TABLE 7

Dehydrochlorination of α-phenethyl chlorides with pyridine

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
Methyl	90	(81)
p-Methyl	73	(94) (91)
2,4-Dimethyl		(94) (91) (198)
2,5-Dimethyl	78	(94)
2,4,5-Trimethyl		(94)
2,4,6-Trimethyl		(94) (91)
p-Ethyl	70	(94) (91)
2,4,5-Triethyl		(94)
Chloro	90	(35)
o-Methoxy	80	(93) (167)
m-Methoxy		(93)
p-Methoxy		(93) (160) (162) (163) (164) (197) (198)
2-Methoxy-5-methyl		(57) (160) (162) (165)
2-Methyl-4-methoxy		(57) (160) (162) (165)
3-Methyl-4-methoxy		(57) (160) (162) (165)

<div align="center">TABLE 7—Continued</div>

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
2-Methoxy-5-isopropyl.....................		(166)
2-Methyl-4-methoxy-5-isopropyl...........		(57) (160) (162) (165)
3,4-Dimethoxy..		(57) (119)
3,4-Methylenedioxy.......................		(9)
p-Ethoxy.		(93)
p-Phenoxy.	17	(57)
Divinylbenzene...........................	82	(35)

Both o- (33) and p-divinylbenzenes (83, 112) have been prepared by distilling the corresponding bis-α-phenethyl bromides with quinoline. The m-isomer was
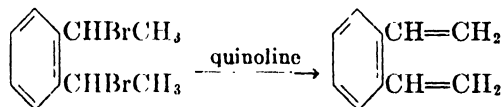
prepared by distilling m-vinyl-α-phenethyl bromide with quinoline (33).

Another convenient method for preparing substituted styrenes is to pyrolyze a quaternary hydroxide. In practice this has been effected either by isolating the

$$ArCH_2CH_2N(CH_3)_3{}^+OH^- \rightarrow ArCH{=}CH_2 + (CH_3)_3N + H_2O$$

quaternary hydroxide and heating it in the dry state or by steam distilling a quaternary halide with a strong base. In table 8 are listed those substituted styrenes which have been prepared in this manner. The yields in this table when listed for a quaternary base invariably are based on the halide precursor. In the preparation of o-dimethylaminomethylstyrene from the quaternary iodide, some N-methyltetrahydroisoquinoline also was isolated (53). The identity of the bis-β-(o-phenylene)ethylamine used as the starting material for the preparation of o-dimethylaminoethylstyrene (21) has been questioned (61). When the methiodide from this o-dimethylaminoethylstyrene was treated with silver oxide and then heated, trimethylamine and a tar were the only products obtained.

The quaternary base and iodide from which p-nitrostyrene was obtained decomposed very easily (78). When (p-nitro-β-phenethyl)dimethylamine was treated with β-phenethyl chloride, the quaternary salt could not be isolated (69). p-Nitrostyrene was obtained directly from the reaction mixture.

2-Carboxy-4,5-dimethoxystyrene has been prepared by heating the methosulfate of the corresponding β-phenethyldimethylamine (101).

$$CH_3O\underset{CH_3O}{\diagdown}\bigcirc\underset{COOH}{\diagup}CH_2CH_2N(CH_3)^+OSO_3CH_3^- \xrightarrow{heat} CH_3O\underset{CH_3O}{\diagdown}\bigcirc\underset{COOH}{\diagup}CH=CH_2$$
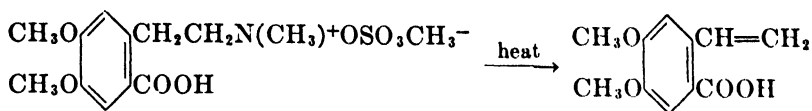
o-Methoxystyrene has been prepared by treating (o-methoxy-β-phenethyl)trimethylammonium iodide with sodium and ethanol.

$$\bigcirc\underset{OCH_3}{\diagdown}CH_2CH_2N(CH_3)_3^+I^- \xrightarrow[C_2H_6OH]{Na} \bigcirc\underset{OCH_3}{\diagdown}CH=CH_2$$
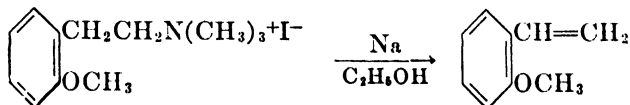
V. DECARBOXYLATION OF CINNAMIC ACIDS

A great many substituted styrenes have been prepared by heating the corresponding cinnamic acids. In table 9 are listed those styrenes which have been

$$ArCH=CHCOOH \rightarrow ArCH=CH_2 + CO_2$$
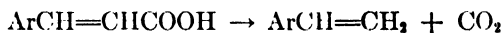
prepared in this manner.

In several cases this decarboxylation has been facilitated by the use of catalysts. These preparations are summarized in table 10.

3-Methoxy-4-hydroxystyrene was obtained in 48 per cent yield by distilling the corresponding cinnamic acid with soda (169). p-Hydroxystyrene was prepared in very low yield by pyrolyzing the barium salt of p-hydroxycinnamic acid (12). 3,4-Carbonyldioxystyrene was obtained in 33 per cent yield by heating 3,4-carbonyldioxycinnamic acid with barium carbonate.

$$\underset{OC}{\overset{O}{\diagdown}}\bigcirc CH=CHCOOH \xrightarrow[170-230°C.]{BaCO_3} \underset{OC}{\overset{O}{\diagdown}}\bigcirc CH=CH_2$$
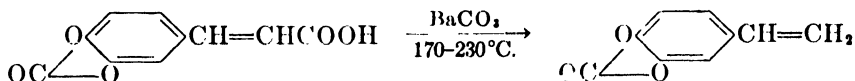
When 3-benzyloxy-4-methoxybenzaldehyde was treated with malonic acid in the presence of pyridine and piperidine, some 3-benzyloxy-4-methoxystyrene was obtained along with the principal product, 3-benzyloxy-4-methoxycinnamic acid (173).

$$\underset{C_6H_5CH_2O}{\overset{CH_3O}{\diagdown}}\bigcirc CHO + CH_2(COOH)_2 \xrightarrow[piperidine]{pyridine}$$

$$\underset{C_6H_5CH_2O}{\overset{CH_3O}{\diagdown}}\bigcirc CH=CH_2 + \underset{C_6H_5CH_2O}{\overset{CH_3O}{\diagdown}}\bigcirc CH=CHCOOH$$
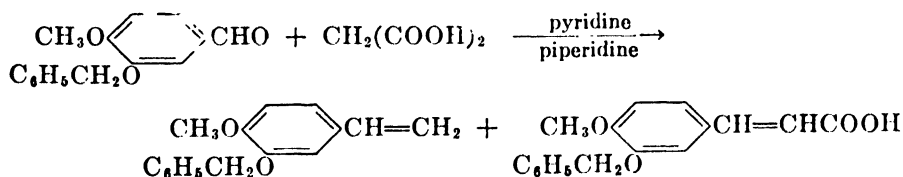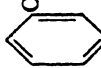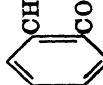
A number of substituted styrenes have been prepared by treating the corresponding halogenated phenylpropionic acid with aqueous sodium carbonate.

$$ArCH=CHCOOH \xrightarrow{HX} ArCHXCH_2COOH \xrightarrow[Na_2CO_3]{aqueous} ArCH=CH_2$$

These preparations are summarized in table 11.

In one preparation, besides the 10 per cent of o-nitrostyrene obtained, there

TABLE 8

Pyrolysis of quaternary hydroxides

STARTING MATERIALS	SUBSTITUTED STYRENE OBTAINED	YIELD *per cent*	REFERENCE
CH_3 (ring) $CH(CH_3)N(CH_3)_2{}^+OH^-$	o-Methyl		(22)
CH_3 (ring) $CH_2CH_2N(CH_3)_3{}^+I^-$ + KOH + H_2O	o-Methyl		(42)
CH_3 (ring) + KOH + CH_3OH, $CH_2CH_2N(CH_3)_3{}^+I^-$	m-Methyl		(212)
H_3C (ring) $CH_2CH_2N(CH_3)_3{}^+I^-$ + KOH + CH_3OH	p-Methyl		(212)
CH_3O (ring) $CH_2CH_2N(CH_3)_3{}^+OH^-$	p-Methoxy	92	(111)
CH_3O (ring) $CH_2CH_2N(CH_3)_3{}^+OH^-$ COOH CH_3O	2-Carboxy-4,5-dimethoxy		(99)
O_2N (ring) $CH_2CH_2N(CH_3)_3{}^+OH^-$	p-Nitro		(78)
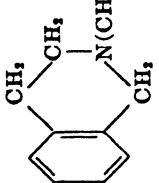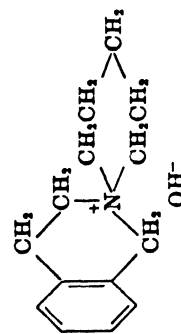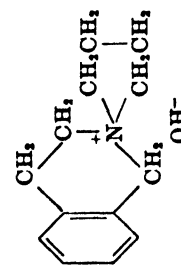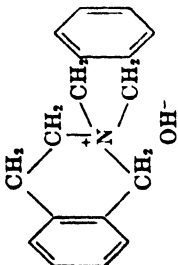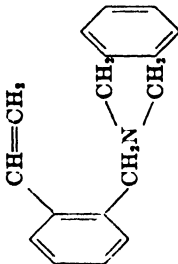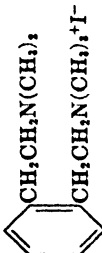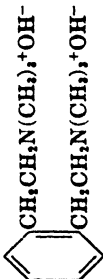
Reactant	Product	Yield, %	Reference
O_2N—C₆H₄—$CH_2CH_2N(CH_3)_3^+I^- + H_2O$	p-Nitro		(78)
$(CH_3)_2N$—C₆H₄—$CH_2CH_2N(CH_3)_3^+OH^-$	p-Dimethylamino	75	(19)
[structure with $N(CH_3)_3^+OH^-$]	o-Dimethylaminomethyl	80, 77	(18), (42)
[structure $N(CH_3)_3^+I^- + KOH + H_2O$]	o-Dimethylaminomethyl		(52, 53)
[structure with CH_2CH_2 OH^-]	[CH=CH₂ structure]		(17)
[structure with CH_2CH_2 OH^-]	[CH=CH₂ structure]		(17)

TABLE 8—*Concluded*

STARTING MATERIALS	SUBSTITUTED STYRENE OBTAINED	YIELD *per cent*	REFERENCE
(benzene ring with CH_3, CH_2–$N^+(CH_2$–$)$ groups, OH^-)	(styrene, $CH=CH_2$ and $CH_2N(CH_2)(CH_2)$)		(17)
$CH_2CH_2N(CH_3)_2$ / $CH_2CH_2N(CH_3)_3{}^+I^-$ $+$ NaOH $+$ H_2O	o-(β-Dimethylaminoethyl)	25–30	(21)
$CH_3CH_2N(CH_3)_3{}^+OH^-$ / $CH_2CH_2N(CH_3)_3{}^+OH^-$	o-Divinylbenzene		(61)

also were isolated 42 per cent of o-nitro-β-hydroxyphenylpropionic acid and 16 per cent of o-nitrocinnamic acid (38).

(10 per cent)

(42 per cent)   (16 per cent)
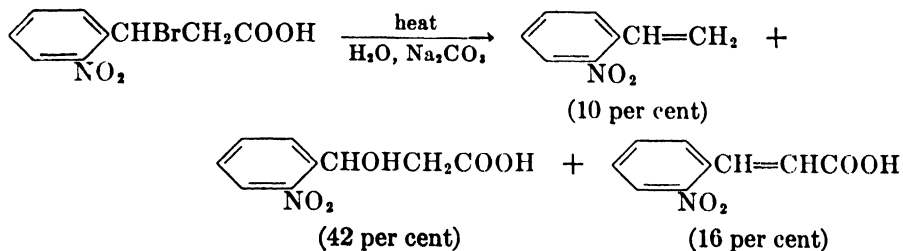
TABLE 9

Decarboxylation of cinnamic acids

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
Isopropyl...		(143)
p-Isopropyl.................		(142)
o-Methoxy.........................		(6)
p-Methoxy........................... {		(143) (144) (145)
o-Hydroxy..................... {	Quantitative 50	(106) (62) (6) (105)
3,4-Dihydroxy......................... {	75	(104) (210)
3-Hydroxy-4-methoxy....................		(211)
3-Methoxy-4-hydroxy......	19	(152)
p-Amino...........................	Almost quantitative	(12)

In a m-nitrostyrene preparation where the yield was 30 per cent, 10 per cent of the β-hydroxyphenylpropionic acid and 20 per cent of the cinnamic acid were isolated (155). In the p-nitrostyrene preparation the yield of p-nitro-β-hydroxyphenylpropionic acid was 65 per cent (10). Some of the β-hydroxyphenylpropionic acid likewise was isolated in the 2-nitro-4-isopropylstyrene preparation (40).

A few substituted styrenes have been prepared by heating the corresponding β-hydroxyphenylpropionic acid lactone alone or in glacial acetic acid. These

$$ArCHCH_2CO \xrightarrow{\text{heat}} ArCH{=}CH_2 + CO_2$$
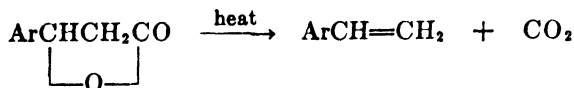
compounds are listed in table 12.

TABLE 10

Catalyzed decarboxylation of cinnamic acids

SUBSTITUTED STYRENE OBTAINED	CATALYST USED	YIELD	REFERENCE
		per cent	
o-Fluoro......................	Quinoline + copper powder	66	(121)
o-Chloro......................	Quinoline + copper sulfate	0	(216)
m-Chloro..................... {	Quinoline + copper powder	86	(216)
	Lepidine + copper sulfate	67	(216)
p-Chloro..................... {	Quinoline + copper powder	83	(216)
	Quinoline + copper acetate	71	(216)
	Lepidine + copper sulfate	58	(216)
	Quinoline + copper sulfate	50–54	(216)
2,4-Dichloro..................	Higher quinoline base + copper powder	20	(216)
3,4-Dichloro.............. .. ... {	Lepidine + copper sulfate	22	(216)
	Higher quinoline base + copper powder	16	(216)
m-Bromo..................... .	Lepidine + copper sulfate	56	(216)
o-Methoxy.................... {	Quinoline + copper powder	67	(216)
	Quinoline + copper powder		(121)
m-Methoxy..................	Copper chromite	27	(77)
p-Methoxy.................. .{	Quinoline + copper powder	85	(216)
	Lepidine + copper sulfate	75	(216)
3,4-Dimethoxy..................	Lepidine + copper sulfate	10	(216)
3-Methoxy-4-hydroxy............	Quinoline + copper powder	74	(169)
3-Methoxy-4-acetoxy............	Quinoline + copper bronze	25	(172)
3,4-Dihydroxy.................	Aniline		(28)
p-Formyl......................	Quinoline + copper powder	52	(219a)
o-Cyano......................	Quinoline + copper bronze	30	(121)
m-Cyano......................	Quinoline + copper powder	51	(219b)
m-Nitro..................... .{	Quinoline + copper powder	60	(219c, 219d)
	Lepidine + copper sulfate	0	(216)
p-Dimethylamino................	Lepidine + copper sulfate	0	(216)
p-Vinyl...	Quinoline + copper powder	45	(219a)

When p-methyl-β-hydroxyphenylpropionic acid was heated with dilute sulfuric acid some p-methylstyrene was isolated along with the main product, p-methylcinnamic acid (4).

TABLE 11

Styrenes from halogenated phenylpropionic acids

SUBSTITUTED STYRENE OBTAINED	HALOGEN IN PHENYL-PROPIONIC ACID	YIELD	REFERENCE
		per cent	
o-Methyl	β-Bromo		(6)
m-Methyl	β-Bromo		(135)
p-Methyl	β-Bromo	51	(5)
Isopropyl	α-Bromo		(143)
p-Isopropyl	β-Bromo		(145)
p-Chloro	β-Bromo		(20)
p-Bromo	β-Bromo		(20)
o-Methoxy	β-Iodo		(148)
	β-Iodo		(147)
	β-Iodo		(146)
p-Methoxy	β-Iodo		(146)
	β-Iodo		(147)
o-Nitro	β-Bromo	10	(38)
	β-Bromo		(98)
	β-Bromo		(150)
m-Nitro	β-Bromo	59	(98)
	β-Bromo	30	(155)
	β-Bromo		(150)
p-Nitro	β-Bromo	29	(10)
2-Nitro-4-isopropyl	β-Bromo		(40)
o-Arsonic acid	β-Bromo		(30)
	β-Bromo		(31)

TABLE 12

Pyrolysis of β-hydroxyphenylpropionic acid lactones

SUBSTITUTED STYRENE OBTAINED	YIELD	REFERENCE
	per cent	
o-Nitro		(38)
m-Nitro		(155)
p-Nitro	70	(98)
		(10)

Reduction of ethyl *p*-nitrocinnamate with tin and hydrochloric acid yielded both *p*-aminocinnamic acid and *p*-aminostyrene (11).

$$O_2N\langle\underline{\quad}\rangle CH{=}CHCOOC_2H_5 \xrightarrow[HCl]{Sn} H_2N\langle\underline{\quad}\rangle CH{=}CHCOOH +$$

$$H_2N\langle\underline{\quad}\rangle CH{=}CH_2$$
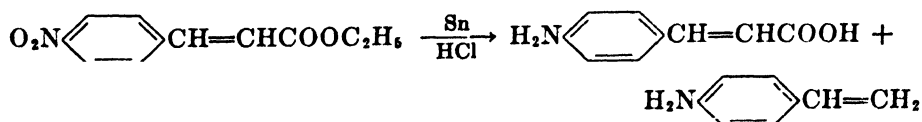
Treatment of 3,4-dibromomethylenedioxycinnamic acid dibromide with aqueous potassium hydroxide has been reported to yield both α- and β-bromo-3,4-dibromomethylenedioxycinnamic acids, 3,4-dibromomethylenedioxystyrene, and 3,4-dibromomethylenedioxy-α-bromostyrene (149).

When α-iodo-β,p-dimethoxyphenylpropionic acid was heated with aqueous ammonia at 100°C., the product was p-methoxystyrene (185).

$$CH_3O\underset{\underset{OCH_3}{|}}{\langle\underline{\quad}\rangle CHCHICOOH} \xrightarrow[100°C.]{NH_3}$$

$$\left[CH_3O\langle\underline{\quad}\rangle CH{=}CHCOOH \right] \longrightarrow CH_3O\langle\underline{\quad}\rangle CH{=}CH_2$$
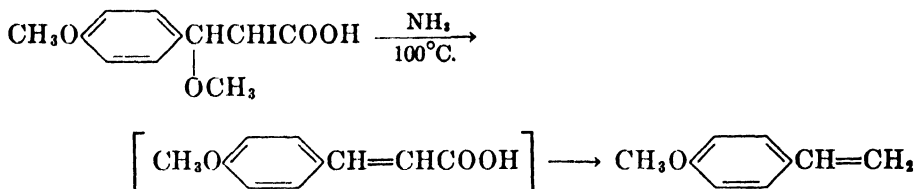
TABLE 13

Dehalogenation of styrene dibromides

SUBSTITUTED STYRENE OBTAINED	DEHALOGENATING AGENT	YIELD	REFERENCE
		per cent	
o-Ethyl............	Mg	70	(61)
2-Hydroxy-3,5-dibromo.	Zn + HCl		(63)
4-Hydroxy-3,5-dibromo	Zn + HBr		(230)
4-Hydroxy-2,3,5-tribromo	Zn + HBr		(231)

Nitration of p-methoxycinnamic acid yielded three products, as shown in the following equation (39):

$$CH_3O\langle\underline{\quad}\rangle CH{=}CHCOOH \xrightarrow[H_2SO_4]{HNO_3} CH_3O\underset{O_2N}{\langle\underline{\quad}\rangle} CH{=}CHCOOH +$$

$$CH_3O\underset{O_2N}{\langle\underline{\quad}\rangle} CH{=}CH_2 + CH_3O\underset{O_2N}{\langle\underline{\quad}\rangle} CH{=}CHNO_2$$
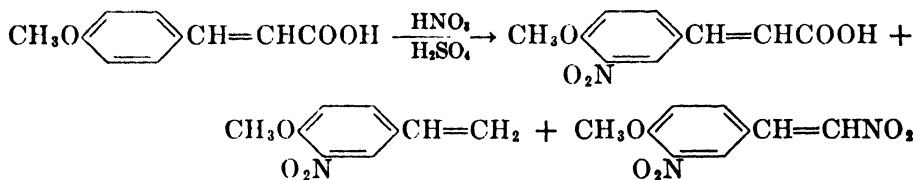
When o-methoxycinnamic acid was treated with sodium hypochlorite, a mixture of mono- and di-chlorinated derivatives of o-methoxystyrene was obtained (148).

VI. MISCELLANEOUS METHODS

A few substituted styrenes have been prepared by treating the corresponding styrene dibromide with a metal or a metal and acid in ether solution. The styrenes prepared in this way are listed in table 13.

$$ArCHBrCH_2Br \xrightarrow{heat} ArCH{=}CH_2$$
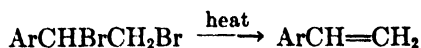
Pyrolysis of the sulfite of 2,4-dimethyl-β-phenethyl alcohol yielded, besides the alcohol, some 2,4-dimethylstyrene (71).

$$\left(H_3C\!\!\left\langle\underline{\quad}\right\rangle\!\!CH_2CH_2O\right)_2 SO \rightarrow H_3C\!\!\left\langle\underline{\quad}\right\rangle\!\!CH_2CH_2OH +$$

$$H_3C\!\!\left\langle\underline{\quad}\right\rangle\!\!CH\!\!=\!\!CH_2$$
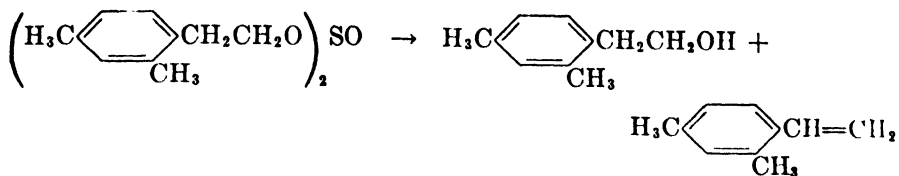
When the vapors of bis(3-methoxy-4-hydroxyphenyl)ethane were passed over "Tonsil" at 230°C., 55 per cent of 3-methoxy-4-hydroxystyrene and 88 per cent of catechol monomethyl ether were obtained (183).

$$\left(HO\!\!\left\langle\underline{\quad}\right\rangle\right)_2 CHCH_3 \rightarrow HO\!\!\left\langle\underline{\quad}\right\rangle\!\!CH\!\!=\!\!CH_2 + HO\!\!\left\langle\underline{\quad}\right\rangle$$

(55 per cent)   (88 per cent)
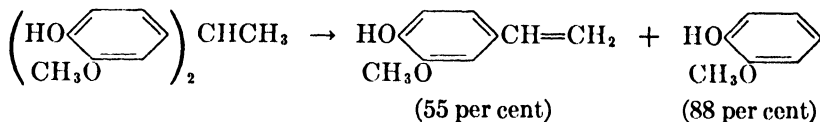
When phenol was treated with vinyl acetate in the presence of concentrated sulfuric acid, o-hydroxystyrene was obtained (137).

$$C_6H_5OH + CH_2\!\!=\!\!CHOCOCH_3 \xrightarrow[H_2SO_4]{conc d.} \left\langle\underline{\quad}\right\rangle\!\!\begin{array}{c}CH\!\!=\!\!CH_2\\OH\end{array}$$

Similarly, treatment of resorcinol with acetylene yielded 83 per cent of 2,4-dihydroxystyrene and 10 per cent of a substituted dibenzopyran (55). 2,4-Di-

$$HO\!\!\left\langle\underline{\quad}\right\rangle^{OH} + HC\!\!\equiv\!\!CH \xrightarrow[CH_3OH]{\begin{array}{c}HgO\\H_2SO_4\end{array}} HO\!\!\left\langle\underline{\quad}\right\rangle^{OH}\!\!CH\!\!=\!\!CH_2 +$$
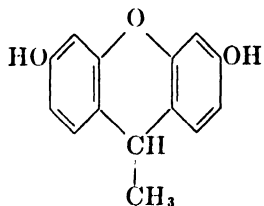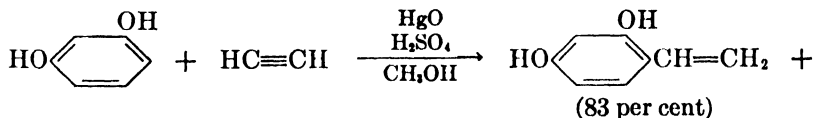
(83 per cent)

methoxystyrene was prepared by the same method.

A mixture of m- and p-vinylphenylisocyanates and 2-methyl-5-vinylphenylisocyanate were prepared in 71 per cent and 31 per cent yields, respectively, by treating the corresponding aminostyrenes with phosgene (103a).

VII. β-NITROSTYRENES

This subject has been reviewed previously to a limited extent (72). β-Nitrostyrene itself was prepared first by Simon in 1839 (190), who obtained it in extremely small yield by distilling styrene with nitric acid. Styrene also has been nitrated by treating its nitrogen trioxide adduct with sulfuric acid (214).

$$C_6H_5CH\!\!=\!\!CH_2 \xrightarrow[CH_3COOH]{NaNO_2} C_6H_5CH\!\!=\!\!CH_2\!\cdot\!N_2O_3 \xrightarrow{H_2SO_4} C_6H_5CH\!\!=\!\!CHNO_2$$
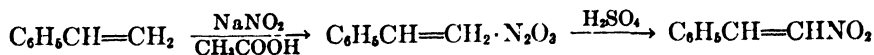
The first satisfactory synthetic method was that of Priebs (1883), who heated benzaldehyde and nitromethane at 160°C. in the presence of zinc chloride (156).

$$C_6H_5CHO + CH_3NO_2 \xrightarrow[160°C.]{ZnCl_2} C_6H_5CH{=}CHNO_2$$
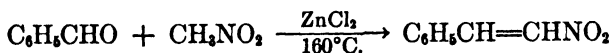
For an 8-hr. run his yield amounted to 30–40 per cent (60 per cent with recycle) (157). He also obtained a 28 per cent yield by nitrating styrene by means of nitrogen pentoxide in ether. It was Priebs who first showed that the nitrostyrene of earlier investigators (3, 13, 190) was β-nitrostyrene. β,o-Dinitrostyrene and β,m-dinitrostyrene have been prepared by Priebs' method (157).

In 1899 Thiele (208) showed that benzaldehyde reacted with nitromethane in the presence of alcoholic potassium hydroxide. The reaction mixture was treated with acid in order to obtain the β-nitrostyrene. Since then this general method has been utilized for the synthesis of a tremendous number of β-nitrostyrenes, either with or without the isolation of the intermediate nitrophenethyl alcohol.

$$ArCHO + CH_3NO_2 \xrightarrow{OH^-} ArCHOHCH_2NO_2 \xrightarrow{H^+} ArCH{=}CHNO_2$$

In table 14 are summarized these β-nitrostyrene preparations.

In one p-acetoxy-β-nitrostyrene preparation, besides the 11 per cent of the product obtained, there also was isolated 15 per cent of p-hydroxy-β-nitrostyrene (68).

In a few instances the intermediate β-nitro-α-phenethyl alcohols have been isolated and used as intermediates for further synthetic work. Since these compounds are so closely related to the β-nitrostyrenes, their preparation is summarized in table 15. In general they are isolated by acidifying the original condensation mixture with acetic acid rather than with a mineral acid.

In the preparation of 3,4-methylenedioxy-β-nitro-α-phenethyl alcohol both the alcohol and 3,4-methylenedioxy-β-nitrostyrene were obtained, as shown in tables 14 and 15 (132). The β,o-dinitro-α-phenethyl alcohol and the β,2,4-trinitro-α-phenethyl alcohol were prepared as intermediates for obtaining the corresponding nitrostyrenes (54). The nitrates of these alcohols were prepared in 75 per cent and 73 per cent yields, respectively, and then converted to the corresponding styrenes by heating in a solvent.

(75 per cent)
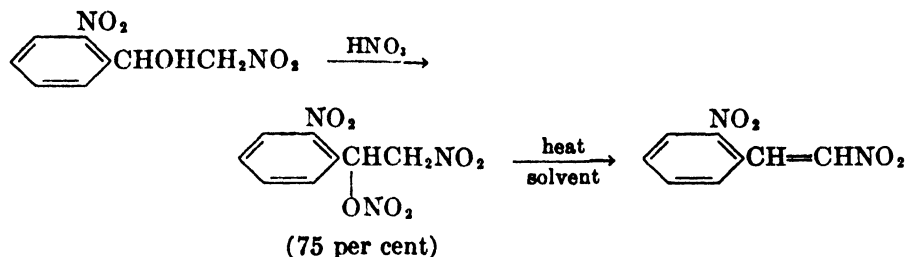
Several investigators tested different condensing and dehydrating agents for the preparation of β-nitrostyrenes. The best yield obtained by the investigator

TABLE 14

β-Nitrostyrenes from aldehydes and nitromethane

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
	NaOH + CH$_3$OH	HCl	80–83	(221)
	C$_2$H$_5$ONa + C$_2$H$_5$OH	Dilute H$_2$SO$_4$	91.5	(75)
	KOH + CH$_3$OH	Dilute H$_2$SO$_4$	80	(209)
	C$_5$H$_{11}$NH$_2$		75	(96)
	KOH + C$_2$H$_5$OH	H$^+$		(208)
	KHCO$_3$	HCl in C$_2$H$_5$OH	14	(89)
p-Methyl..............	C$_5$H$_{11}$NH$_2$		60	(223)
o-Fluoro..............	(C$_2$H$_5$)$_3$N		60	(228)
o-Chloro.............	(C$_2$H$_5$)$_3$N		70	(222)
	(C$_2$H$_5$)$_3$N			(224)
	NaOH + CH$_3$OH	HCl	Good	(27)
m-Chloro..............	NaOH + CH$_3$OH	HCl	Good	(27)
p-Chloro.............	NaOH + CH$_3$OH	HCl	Good	(27)
	KOH + C$_2$H$_5$OH	Dilute HCl		(170)
o-Bromo.............	(C$_2$H$_5$)$_3$N		60	(227)
	Piperidine + C$_4$H$_9$NH$_2$		50	(27)
m-Bromo..............	KOH + CH$_3$OH	HCl		(100)
p-Bromo..............	C$_5$H$_{11}$NH$_2$		67	(222)
o-Iodo................	(C$_2$H$_5$)$_3$N		65–70	(226)
o-Nitro..............	CH$_3$ONa + CH$_3$OH	ZnCl$_2$ in CH$_3$COOH		(16)
	CH$_3$ONa + CH$_3$OH	ZnCl$_2$ in CH$_3$COOH		(15)
m-Nitro.............	KOH + H$_2$O + C$_2$H$_5$OH	Concentrated HCl	76	(194)
	(C$_2$H$_5$)$_3$N		47	(222)
	KOH + C$_2$H$_5$OH	H$^+$		(208)
	KOH + C$_2$H$_5$OH	HCl		(32)
p-Nitro................	KOH + C$_2$H$_5$OH	H$^+$		(208)
m-Cyano.............	KOH + H$_2$O + C$_2$H$_5$OH	HCl	43	(192)
m-Carbomethoxy......	KOH + H$_2$O + C$_2$H$_5$OH	HCl	70	(192)
m-Carbethoxy.........	KOH + H$_2$O + C$_2$H$_5$OH	HCl	63	(192)
p-Carbomethoxy.......	KOH + H$_2$O + C$_2$H$_5$OH	HCl	62	(192)
p-Carbethoxy.........	KOH + H$_2$O + C$_2$H$_5$OH	HCl	64	(192)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
o-Hydroxy	NaOH + H₂O + CH₃OH	HCl	35	(68)
	KOH + C₂H₅OH	Dilute HCl		(170)
2-Hydroxy-3-nitro	KOH + C₂H₅OH	Dilute HCl		(170)
2-Hydroxy-3-carboxy	KOH + C₂H₅OH	Dilute HCl		(170)
2-Hydroxy-3-carbethoxy	KOH + C₂H₅OH	Dilute HCl	0	(170)
2 Hydroxy-3-carboxy-5-nitro	KOH + C₂H₅OH	Dilute HCl	0	(170)
o-Methoxy	(C₂H₅)₃N			(225)
m-Hydroxy	NaOH + H₂O + CH₃OH	HCl	66	(68)
	KOH + C₂H₅OH	Dilute HCl		(170)
m-Methoxy	KOH + H₂O + CH₃OH	Dilute H₂SO₄		(187)
m-Carbethoxymethyl-eneoxy	KOH + C₂H₅OH	Dilute HCl		(170)
m-Carboxymethyl-eneoxy	KOH + C₂H₅OH	Dilute HCl	0	(170)
p-Hydroxy	KOH + C₂H₅OH	Dilute HCl	0	(170)
3-Nitro-4-hydroxy	KOH + C₂H₅OH	Dilute HCl	0	(170)
3-Carbethoxy-4-hydroxy	KOH + C₂H₅OH	Dilute HCl	0	(170)
3-Carboxy-4-hydroxy-5-nitro	KOH + C₂H₅OH	Dilute HCl	0	(170)
p-Methoxy	(CH₃NH₃)₂CO₃		86	(96)
	CH₃ONa + CH₃OH	ZnCl₂ in CH₃COOH	80	(16)
	KOH + C₂H₅OH	10% HCl	76	(102)
	KOH + C₂H₅OH	H⁺	68	(174)
	C₅H₁₁NH₂		62	(222)
	C₂H₅ONa	HCl		(86)
	CH₃ONa + CH₃OH	ZnCl₂ in CH₃COOH		(15)
	(CH₃NH₃)₂CO₃			(95)
3-Bromo-4-methoxy	KOH + C₂H₅OH	HCl		(100)
3-Nitro-4-methoxy	KOH + H₂O + C₂H₅OH	Concentrated HCl	74	(194)
	KOH + C₂H₅OH	Dilute HCl		(170)
p-Benzyloxy	CH₃ONa + CH₃OH	Dilute HCl		(176)
p-Acetoxy	NaOH + H₂O + CH₃OH	HCl	11	(68)
	KOH + C₂H₅OH	Dilute HCl		(170)
2-Nitro-5-acetoxy	KOH + C₂H₅OH	(CH₃CO)₂O + CH₃COONa	82	(10a)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
2-Nitro-6-acetoxy......	KOH + C_2H_5OH	$(CH_3CO)_2O$ + CH_3COONa	Almost theoretical	(10a)
p-Benzoxy........... {	KOH + C_2H_5OH	Dilute HCl		(170)
	CH_3ONa + CH_3OH	Dilute HCl		(176)
p-Ethoxycarboxy..... {	CH_3ONa + CH_3OH	Dilute HCl		(177)
	CH_3ONa + CH_3OH	Dilute HCl		(176)
p-Carboxymethyl-eneoxy.............	KOH + C_2H_5OH	Dilute HCl	0	(170)
p-Carbethoxymethyl-eneoxy.............	KOH + C_2H_5OH	Dilute HCl		(170)
2-Hydroxy-4-methoxy..	CH_3COONH_4 + C_2H_5OH	Dilute H_2SO_4	Good	(168)
2,4-Dimethoxy .... {	CH_3COONH_4 + C_2H_5OH	Dilute H_2SO_4	Good	(168)
	KOH + CH_3OH	Dilute H_2SO_4		(117)
2,4-Dimethoxy-5-nitro.	CH_3NH_2		Good	(168)
2-Ethoxy-4-methoxy...	CH_3COONH_4 + C_2H_5OH	Dilute H_2SO_4	Good	(168)
2,5-Dimethoxy........	$(CH_3NH_3)_2CO_3$		76	(205)
3,4-Dihydroxy........	KOH + C_2H_5OH	Dilute HCl	0	(170)
3-Hydroxy-4-methoxy .	NaOH + H_2O + CH_3OH	HCl	96	(67)
3-Methoxy-4-hydroxy {	$(CH_3NH_3)_2CO_3$		90	(96)
	NaOH + CH_3OH		84	(68)
	$C_5H_{11}NH_2$		80	(222)
	CH_3ONa	HCl		(177)
	CH_3COONH_4 + C_2H_5OH	Dilute H_2SO_4	Good	(168)
3-Methoxy-4-hydroxy-5-bromo.............	CH_3NH_2		73	(115)
3,4-Dimethoxy....... {	$(CH_3NH_3)_2CO_3$	CH_3COOH	83	(191)
	KOH + CH_3OH	HCl	68	(175)
	KOH + C_2H_5OH	Dilute HCl		(173)
	KOH + CH_3OH	Dilute HCl		(99)
	KOH + CH_3OH	Dilute HCl		(101)
	CH_3ONa	HCl		(8)
3,4-Dimethoxy-5-bromo..............	KOH + C_2H_5OH		41	(213)
3,4-Dimethoxy-5-nitro .	KOH + H_2O + C_2H_5OH	Concentrated HCl	76	(194)

TABLE 14—*Continued*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
3-Methoxy-4-ethoxy	$KOH + H_2O + C_2H_5OH$	Dilute HCl	100	(201)
	$KOH + CH_3OH$	10 per cent HCl		(103)
				(182)
3,4-Diethoxy	$(CH_3NH_3)_2CO_3$	CH_3COOH	94	(191)
3-Methoxy-4-benzyl-oxy	$NaOH + C_2H_5OH$	HCl	97	(107)
	CH_3NH_2		89	(97)
	$KOH + H_2O + C_2H_5OH$	10 per cent HCl	88	(202)
3-Benzyloxy-4-meth-oxy	$(CH_3NH_3)_2CO_3$		85	(173)
	$KOH + H_2O + C_2H_5OH$	10 per cent HCl	40	(202)
3-Methoxy-4-methoxy-methyleneoxy	$(CH_3NH_3)_2CO_3$			(97)
	$C_5H_{11}NH_2$		96	(222)
	$(CH_3NH_3)_2CO_3$	CH_3COOH	94	(191)
	OH^-	Dilute HCl	93	(207)
	$(CH_3NH_3)_2CO_3$		93	(96)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH	75	(16)
3,4-Methylenedioxy	$NaOH + C_2H_5OH$	HCl	74	(107)
	$KOH + C_2H_5OH$	Dilute H_2SO_4	38	(136)
	$KHCO_3$	HCl in C_2H_5OH	34	(89)
	$CH_3ONa + CH_3OH$	$ZnCl_2$ in CH_3COOH		(15)
	$CH_3ONa + CH_3OH$	H^+		(132)
	$KOH + CH_3OH$	HCl		(175)
3-Methoxy-4-acetoxy	$KHCO_3$	HCl in C_2H_5OH	27	(89)
3-Methoxy-4-benzoxy	$(CH_3NH_3)_2CO_3$		75	(213)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
3,4-Diacetoxy	$KHCO_3$	HCl in C_2H_5OH	70	(89)
3,4-Dibenzoxy	$CH_3ONa + CH_3OH$	Dilute HCl		(177)
	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
3,4-Di(ethoxycarboxy)	$CH_3ONa + CH_3OH$	Dilute HCl		(176)
2,3,4-Trimethoxy	$KOH + C_2H_5OH$	Dilute HCl	73	(193)
2,4,5-Trimethoxy	$KOH + H_2O + C_2H_5OH$	HCl		(85)
	$KOH + H_2O + C_2H_5OH$	HCl		(86)

TABLE 14—*Concluded*

SUBSTITUTED β-NITROSTYRENE OBTAINED	ALKALINE CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
3,5-Dimethoxy-4-hydroxy..............	KOH + C_2H_5OH			(130)
3,4,5-Trimethoxy.....	KOH + C_2H_5OH	10 per cent HCl	80	(200)
	KOH + C_2H_5OH	Dilute HCl	79	(193)
	KOH + C_2H_5OH			(130)
3,4,5-Triethoxy.......	KOH + C_2H_5OH	Dilute HCl	55	(193)
2,5-Dimethoxy-3,4-methylenedioxy......	KOH + CH_3OH			(117)

in question has been given in table 14. In table 16 are shown for purposes of comparison the various conditions tried.

Worrall (222) showed that β-nitro-α-phenethyl alcohol was converted quantitatively to β-nitrostyrene by distillation from acids. The use of molar quantities of diethylamine or amylamine in the benzaldehyde–nitromethane reaction gave only tar. Good yields of β-nitrostyrene were obtained from nitromethane and benzalbutylamine or benzalamylamine. Nitromethane reacted with benzalaniline to give an adduct which yielded β-nitrostyrene on heating with hydrochloric acid (131).

$$C_6H_5CH{=}NC_6H_5 \ + \ CH_3NO_2 \ \rightarrow \ C_6H_5\underset{\underset{NHC_6H_5}{|}}{C}HCH_2NO_2 \ \rightarrow \ C_6H_5CH{=}CHNO_2$$
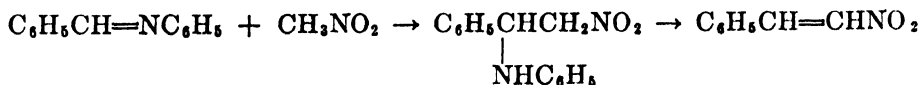
Treatment of this adduct with benzaldehyde also gave β-nitrostyrene (222).

$$C_6H_5\underset{\underset{NHC_6H_5}{|}}{C}HCH_2NO_2 \ + \ C_6H_5CHO \ \rightarrow$$

$$C_6H_5CH{=}CHNO_2 \ + \ C_6H_5CH{=}NC_6H_5 \ + \ H_2O$$
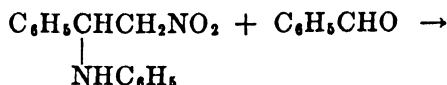
Quite a few β-nitrostyrenes have been prepared by nitrating cinnamic acids.

$$ArCH{=}CHCOOH \ \xrightarrow{HNO_3} \ ArCH{=}CHNO_2$$

The aromatic nucleus may or may not be nitrated in the process. The β-nitrostyrenes prepared by this means are listed in table 17.

Nitric acid or a mixture of nitric and sulfuric acids was used for all of these nitrations except in the case of cinnamic acid itself, where nitrogen dioxide in ether (49), hot aqueous sodium nitrate (49), and nitrous and sulfuric acids (154) were found to be effective.

In the nitration of *o*-methylcinnamic acid, some 2-methyl-4-nitrocinnamic acid was obtained as well as the 2-methyl-β,4-dinitrostyrene (58). Likewise, as
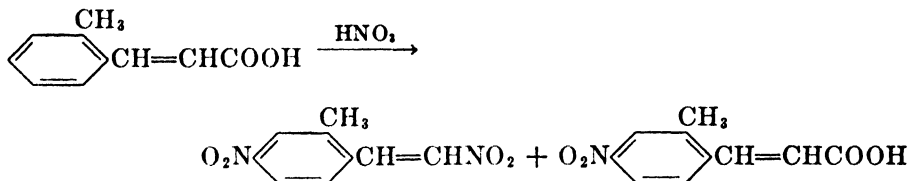
mentioned in a previous section, the nitration of *p*-methoxycinnamic acid yielded, besides 4-methoxy-β,3-dinitrostyrene, 3-nitro-4-methoxystyrene and 3-nitro-4-methoxycinnamic acid (151).

TABLE 15

β-Nitro-α-phenethyl alcohols

SUBSTITUTED β-NITRO-α-PHENETHYL ALCOHOL OBTAINED	CONDENSING AGENT	YIELD	REFERENCE
		per cent	
	CH_3ONa	84	(76)
	$CH_3ONa + CH_3OH$		(176)
o-Nitro	$(C_2H_5)_3N$		(54)
	$KOH + C_2H_5OH$		(208)
2,4-Dinitro.........................	$(C_2H_5)_3N$	41	(54)
p-Methoxy.........................	$CH_3ONa + CH_3OH$		(176)
3,5-Dinitro-4-methoxy.................	$KOH + C_2H_5OH$		(170)
p-Benzoxy........................	$CH_3ONa + CH_3OH$		(176)
p-Ethoxycarboxy....................	$CH_3ONa + CH_3OH$		(176)
2,5-Dihydroxy.......................	$CH_3ONa + CH_3OH$		(170)
3,4-Dihydroxy.......................	$NaHSO_3 + NaOH + H_2O$	93	(88)
3,4-Dimethoxy.......................	$CH_3ONa + CH_3OH$		(176)
3,4-Methylenedioxy..................	CH_3ONa		(132)
3,4-Dibenzoxy.......................	$CH_3ONa + CH_3OH$		(176)
3,4-Di(ethoxycarboxy)................	$CH_3ONa + CH_3OH$		(176)

These cinnamic acid nitrations are believed to proceed through an intermediate of the type:

$$\left(ArCH{=}C\stackrel{\textstyle NO_2}{\diagdown COOH} \right)$$
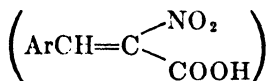
which loses carbon dioxide on treatment with water (109). Treatment of such a compound with concentrated sulfuric acid below 10°C. yielded the corresponding β-nitrostyrene (60).
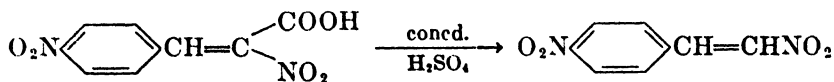
TABLE 16

Comparison of β-nitrostyrene preparations

SUBSTITUTED β-NITRO-STYRENE OBTAINED	CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFERENCE
			per cent	
	5% concentrated aqueous NH_3		14	(222)
	5% hydrobenzamide		14	(222)
	5% n-$C_4H_9NH_2$		54	(222)
	5% $HOCH_2CH_2NH_2$		54	(222)
	5% $CH_2{=}CHCH_2NH_2$		57	(222)
	5% $C_6H_5CH_2NH_2$		61	(222)
	5% n-$C_5H_{11}NH_2$		64	(222)
	5% piperidine		14	(222)
	5% pyridine		Trace	(222)
	5% $(C_2H_5)_2NH$		38	(222)
	5% $(C_6H_5CH_2)_2NH$		Poor	(222)
	5% $(n$-$C_4H_9)_2NH$		Poor	(222)
	5% $(HOCH_2CH_2)_2NH$		Poor	(222)
	5% $(C_2H_5)_3N$		52	(222)
	5% $(HOCH_2CH_2)_3N$		53	(222)
	10% $C_6H_5NH_2$		32	(222)
	10% o-toluidine		4	(222)
	10% m-toluidine		38	(222)
	10% p-toluidine		41	(222)
	10% p-chloroaniline		23	(222)
	10% p-anisidine		57	(222)
	10% p-aminodimethylaniline		54	(222)
	10% α-naphthylamine		<1	(222)
	10% β-naphthylamine		24	(222)
	$C_5H_{11}NH_2$		75	(96)
	$C_2H_5NH_2$		25	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)
o-Chloro............	$C_5H_{11}NH_2$		3-4	(222)
	$(C_2H_5)_2NH$		50	(222)
	$(C_2H_5)_3N$		70	(222)
p-Bromo..........	$C_5H_{11}NH_2$		67	(222)
	$(C_2H_5)_3N$		50	(222)
m-Nitro............	$C_5H_{11}NH_2$		9	(222)
	$(C_2H_5)_3N$		47	(222)
	$KOH + H_2O + C_2H_5OH$	Concentrated HCl	76	(194)
	CH_3NH_2		32	(194)
p-Carbomethoxy....	$KOH + H_2O + C_2H_5OH$	HCl	62	(192)
	CH_3NH_3Cl		33	(192)
o-Hydroxy..........	$NaOH + H_2O + CH_3OH$	HCl	35	(68)
	$CH_3NH_2 \cdot CH_3COOH$		28	(68)

TABLE 16—*Concluded*

SUBSTITUTED β-NITRO-STYRENE OBTAINED	CONDENSING AGENT	DEHYDRATING AGENT	YIELD	REFER-ENCE
			per cent	
p-Methoxy.........	$C_5H_{11}NH_2$		62	(222)
	$(C_2H_5)_3N$		39	(222)
	$(CH_3NH_3)_2CO_3$		86	(96)
	KOH + CH_3OH	H^+	65	(96)
	$C_2H_5NH_2$		0	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)
2-Hydroxy-4-meth-oxy..............	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
	CH_3NH_3Cl		Low	(168)
3-Methoxy-4-hy-droxy.	$(CH_3NH_3)_2CO_3$		90	(96)
	KOH + CH_3OH	H^+	0	(96)
	$C_2H_5NH_2$		0	(96)
	$C_5H_{11}NH_2$		80	(222)
	$(C_2H_5)_3N$		0	(222)
	$CH_3COONH_4 + C_2H_5OH$	Dilute H_2SO_4	Good	(168)
	CH_3NH_4Cl		Good	(168)
3,4-Dimethoxy-5-nitro	KOH + H_2O + C_2H_5OH	Concentrated HCl	76	(194)
	CH_3NH_2		30	(194)
3,4-Methylenedioxy.	$C_5H_{11}NH_2$		80	(222)
	$(C_2H_5)_3N$		0	(222)
	KOH + CH_3OH	H^+	95	(96)
	$(CH_3NH_3)_2CO_3$		93	(96)
	$C_2H_5NH_2$		25	(96)
	$(C_2H_5)_2NH$		0	(96)
	Piperidine		0	(96)

Nitration of *m*- and *p*-nitrostyryl methyl ketones and of *m*- and *p*-nitrodistyryl ketones yielded the corresponding β-nitrostyrenes (110). In the case of the

$$O_2N\text{—}\langle\text{—}\rangle\text{—}CH{=}CHCOCH_3 \xrightarrow{HNO_3} O_2N\text{—}\langle\text{—}\rangle\text{—}CH{=}CHNO_2$$
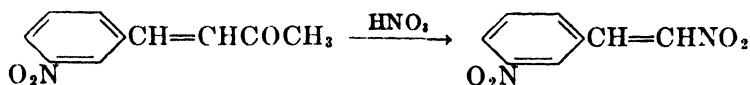
p-nitrodistyryl ketone an intermediate nitro compound was isolated which decomposed to give β,*p*-dinitrostyrene on treatment with water.

$$O_2N\text{—}\langle\text{—}\rangle\text{—}CH{=}CHCOCH{=}CH\text{—}\langle\text{—}\rangle\text{—}NO_2 \xrightarrow[HNO_3]{absolute}$$

$$O_2N\text{—}\langle\text{—}\rangle\text{—}\underset{O_2N}{CH}{=}\underset{NO_2}{C}COC{=}CH\text{—}\langle\text{—}\rangle\text{—}NO_2 \xrightarrow{H_2O}$$

$$2\,O_2N\text{—}\langle\text{—}\rangle\text{—}CH{=}CHNO_2$$
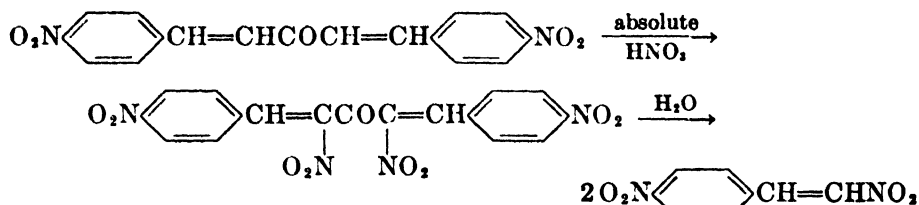
A similar compound derived from *p*-methoxystyryl methyl ketone decomposed on treatment with aqueous sodium hydroxide to give *p*-methoxy-β-nitrostyrene (218).

$$CH_3O\langle\!\!\!=\!\!\!\rangle CH=\!\!\underset{\underset{NO_2}{|}}{C}COCH_3 \xrightarrow[H_2O]{NaOH} CH_3O\langle\!\!\!=\!\!\!\rangle CH=CHNO_2$$
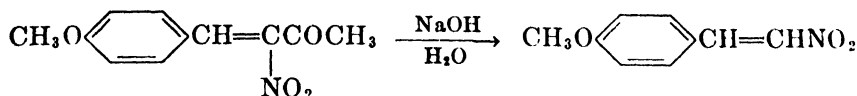
TABLE 17
β-Nitrostyrenes by nitration of cinnamic acids

SUBSTITUTED CINNAMIC ACID USED	SUBSTITUTED β-NITROSTYRENE OBTAINED	YIELD	REFERENCE
		per cent	
		38	(154)
		15	(49)
			(48)
	(o + p)-Nitro		(109)
o-Methyl..........................	2-Methyl-4-nitro		(58)
p-Methyl..........................	3-Nitro-4-methyl		(70)
p-Chloro..........................	(2 + 3)-Nitro-4-chloro	67	(109)
p-Bromo..........................	(2 + 3)-Nitro-4-bromo	66	(109)
3,4,5-Tribromo....................	2-Nitro-3,4,5-tribromo		(25)
o-Nitro..........................	o-Nitro	50	(109)
	o-Nitro		(108)
m-Nitro..........................	m-Nitro	70	(109)
	m-Nitro		(59)
p-Nitro..........................	p-Nitro	75	(109)
	p-Nitro	22	(151)
2-Nitro-4-chloro..................	2-Nitro-4-chloro	60	(109)
3-Nitro-4-chloro..................	3-Nitro-4-chloro	60	(109)
2-Nitro-4-bromo..................	2-Nitro-4-bromo	70	(109)
3-Nitro-4-bromo..................	3-Nitro-4-bromo.	70	(109)
p-Methoxy........................	3-Nitro-4-methoxy		(39)
p-Amino..........................	2-Nitro-4-amino		(59)
p-Acetamino......................	3-Nitro-4-acetamino		(65)

α-Ethoxy-β-nitrostyrene was obtained in 25–30 per cent yields by a similar procedure (217).

$$C_6H_5\underset{\underset{C_2H_5O}{|}}{C}H\underset{\underset{NO_2}{|}}{C}HCOC_6H_5 \xrightarrow[C_2H_5OH]{KOH} C_6H_5\underset{\underset{OC_2H_5}{|}}{C}=CHNO_2$$

A dinitro derivative behaved similarly (219).

$$C_6H_5\underset{\underset{O_2N}{|}}{C}H\underset{\underset{NO_2}{|}}{C}HCOCH=CHC_6H_5 \xrightarrow[CH_3OH]{KOH}$$

$$C_6H_5CH=CHNO_2 + NH_4NO_2 + C_6H_5CH=CHCOOH$$
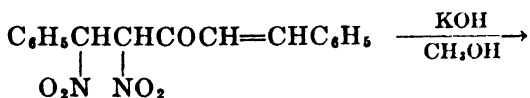
Sodium nitromethane reacted with benzil in ethanol solution to give ethyl benzoate and sodium β-nitro-α-phenethyl alcohol (64, 90). The latter compound yielded β-nitrostyrene on treatment with acid. Yields of 56–58 per cent were obtained (64).

$$C_6H_5COCOC_6H_5 + CH_2\!\!=\!\!NO_2Na + C_2H_5OH \rightarrow$$

$$C_6H_5COOC_2H_5 + C_6H_5CHOHCH\!\!=\!\!NO_2Na \xrightarrow{\ H^+\ } C_6H_5CH\!\!=\!\!CHNO_2$$
$$\text{(58 per cent)} \hspace{8em} \text{(56 per cent)}$$
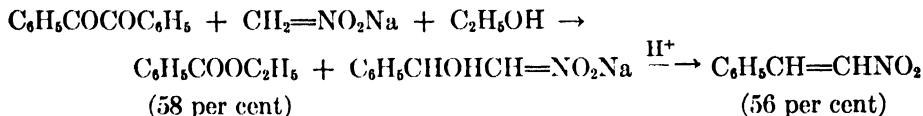
Under the same conditions (nitromethane and sodium ethoxide in pyridine) phenyl furyl diketone yielded β-nitrostyrene, ethyl benzoate, and ethyl furoate but no α-furyl-β-nitroethylene (64).

Nitromethane reacted with the quinoid forms of vanillylidenemethylamine and of 5-bromovanillylidenemethylamine to give methylamine salts of the corresponding β-nitrostyrenes (115). Treatment with hydrochloric acid liberated the β-nitrostyrene.
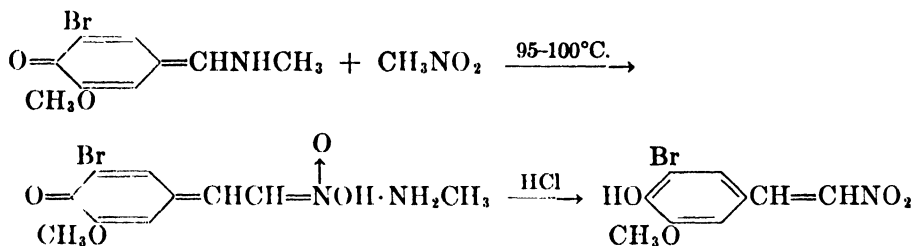
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CLEAVAGES AND REARRANGEMENTS INVOLVING OXYGEN RADICALS AND CATIONS

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CONTENTS

I. INTRODUCTION

In the decomposition of organic peroxides, rupture of the bond between the two peroxidic oxygens is often accompanied by cleavage of an adjacent carbon-to-carbon bond. Such cleavage is not an unusual feature of reactions involving oxygen radicals or oxygen cations. This generalization, which is supported by numerous examples, is a very useful one, casting light on the mechanisms of a number of reactions.

The reactions to be discussed can be formulated as involving either oxygen cations or oxygen free-radicals. A choice between the two mechanisms can often be made on the basis of the reaction conditions, the catalysts, and the products of the reaction. When there is more than one carbon-to-carbon bond next to the unsaturated oxygen, the bond that breaks furnishes a clue to the state of the oxygen. Thus, if the oxygen bears a positive charge, the bond that breaks preferentially is the one leading to that group which would migrate preferentially within a carbonium ion. If the oxygen bears an odd electron instead of a positive charge, the order of bond cleavage is different.

II. PEROXIDE DECOMPOSITION

A. Diacyl peroxides

The decarboxylation of diacyl peroxides is an example of the type of cleavage under consideration, and in most cases is of the free-radical type. When a diaroyl peroxide decomposes in an aromatic solvent, a diaryl is formed by attack of radicals from the peroxide on the solvent.

$$\underset{\substack{\|\\ \text{Ar}\overset{O}{C}}}{}\!\!-\!\text{OO}\!-\!\underset{\substack{\|\\ \overset{O}{C}\text{Ar}}}{}\;\longrightarrow\; 2\text{Ar}\overset{O}{\underset{\|}{C}}\text{O}\cdot$$

$$\text{R}\cdot\; +\; \text{Ar}\overset{O}{\underset{\|}{C}}\text{O}\cdot\; +\; \text{Ar}'\text{H}\;\longrightarrow\; \text{RH}\; +\; \text{ArAr}'\; +\; \text{CO}_2$$
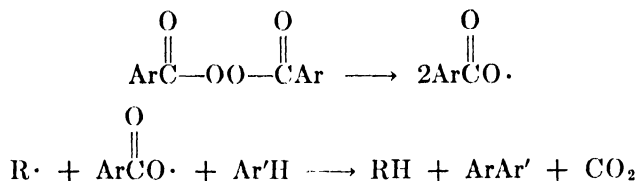
That the attacking fragment is a free radical rather than a positive ion is shown by the invariably ortho- and para-directive effect of various substituents on the solvent nucleus (32, 37, 50, 74). Benzoyl peroxide in nitrobenzene at 74°C. gives o- and p-nitrodiphenyls (74). Since the nitro group would direct a positive fragment of the peroxide to a meta position, the radical rather than the cationic interpretation is preferred.

Furthermore, the alkoyloxy moiety of an unsymmetrical peroxide in general loses its carbon dioxide more readily than does the aroyloxy part (73, 74). The benzoxy half of an unsymmetrical peroxide in turn loses its carbon dioxide more readily than does a substituted benzoxy moiety; this is true whatever the substituent (73). Such behavior is incompatible with an ionic mechanism but does not clash with the view that free radicals are involved. The substituents tested (73) were phenyl, chloro, methoxy, and nitro, all in the para position. If the mechanism were cationic, it would be reasonable to expect the methoxy group to increase and the nitro group to decrease decarboxylation. Substituents should act as they do on the migration aptitude of groups migrating within a carbonium ion. Positive ions are therefore not intermediate in the decomposition of diacyl peroxides under ordinary conditions.

The free-radical mechanism accounts quite well for the effect of substituents on decarboxylation, as will be seen by inspection of the following stabilizing resonance structures:
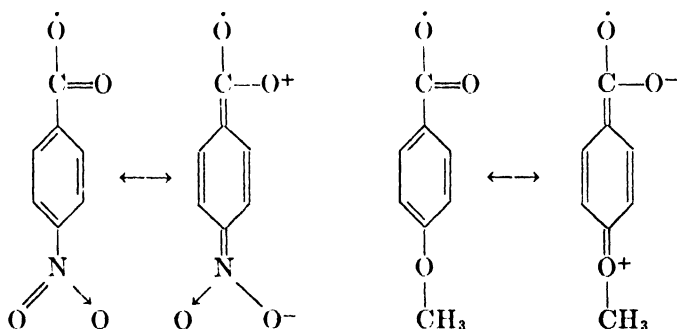
The evidence cited above makes it clear that free radicals are formed when diacyl peroxides decompose in the pure state or in neutral media. But at least two diacyl peroxides, phenylacetyl and benzoyl peroxides, are subject to a general acid catalysis of their decomposition (5). The stronger the acid, the faster is the decomposition induced by it. The acid-catalyzed part of the reaction presumably involves positive ions:

$$\underset{\displaystyle \text{RCOOCR}}{\overset{\displaystyle \text{O} \quad \text{O}}{\| \quad \|}} \xrightarrow{\text{H}^+} \left[\underset{+}{\overset{\displaystyle \text{OH} \quad \text{O}}{\underset{\displaystyle \text{RCOOCR}}{| \quad \|}}} \right] \longrightarrow \text{RCOO}^+ + \text{RCOOH} \xrightarrow{\text{B}^-} \begin{cases} \text{RB} + \text{CO}_2 \\ \quad \text{or} \\ \text{RCOOB} \end{cases}$$
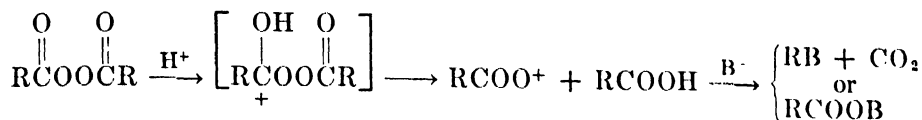
B. Dialkyl peroxides

The dialkyl peroxides provide numerous examples of the cleavage of carbon-to-carbon bonds adjacent to the oxygen–oxygen bond. The generality of this reaction for tertiary alkyl peroxides has been pointed out by George and Walsh (33):

$$\underset{\underset{\displaystyle \text{R}}{|}}{\overset{\overset{\displaystyle \text{R}}{|}}{\text{R---C---O}}} \vdots \overset{\overset{\displaystyle \text{R}}{|}}{\underset{\underset{\displaystyle \text{R}}{|}}{\text{O---C---R}}} \xrightarrow{\text{heat}} 2\text{R}\cdot + 2\text{R}_2\text{CO}$$

$$2\text{R}\cdot \longrightarrow \text{RR}$$
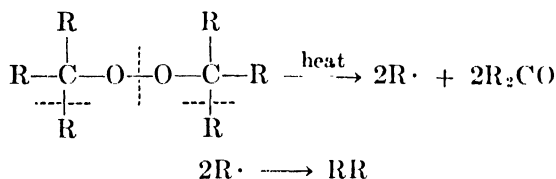
Twelve examples are given in table 1; most of them are vapor-phase reactions and hence free-radical rather than ionic. They fit the scheme given above or a variant of it. In the case of Wieland's triphenylmethyl peroxide (reaction 7 of table 1), the driving force seems to be resonance stabilization of a free radical rather than carbonyl formation.

$$(\text{C}_6\text{H}_5)_3\text{COOC}(\text{C}_6\text{H}_5)_3 \longrightarrow [2(\text{C}_6\text{H}_5)_3\text{C---O}\cdot] \longrightarrow 2(\text{C}_6\text{H}_5)_2\text{C---OC}_6\text{H}_5]$$

$$2 \left[\underset{\displaystyle \cdot}{\overset{\overset{\displaystyle \text{C}_6\text{H}_5}{|}}{\text{C}_6\text{H}_5\text{COC}_6\text{H}_5}} \right] \longrightarrow \underset{\underset{\displaystyle \text{C}_6\text{H}_5}{|}}{\overset{\overset{\displaystyle \text{C}_6\text{H}_5\text{O}}{|}}{\text{C}_6\text{H}_5\text{C}}}\text{-------}\underset{\underset{\displaystyle \text{C}_6\text{H}_5}{|}}{\overset{\overset{\displaystyle \text{OC}_6\text{H}_5}{|}}{\text{CC}_6\text{H}_5}}$$
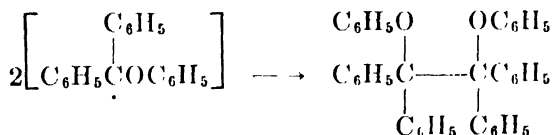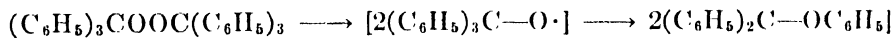
In the cyclic enol peroxides (reactions 9–12) only one carbon bond breaks; it is adjacent to both of the peroxide oxygens.

$$\tag{31}$$
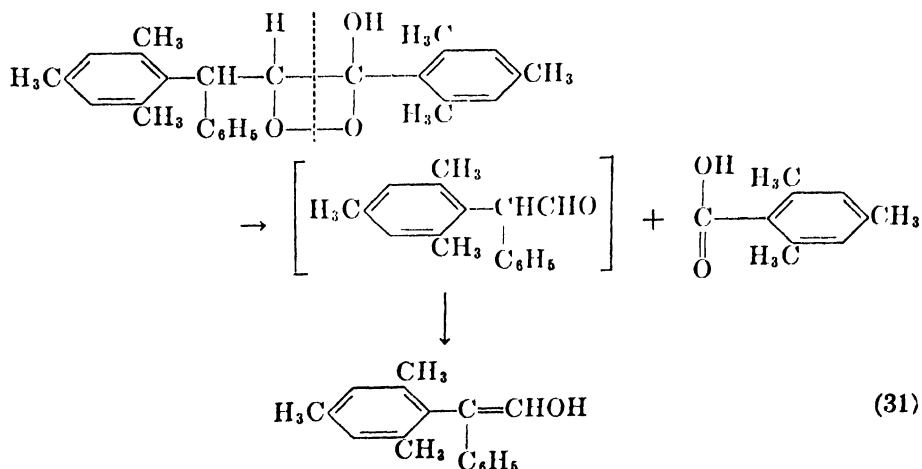
TABLE 1

Decomposition of alkyl peroxides
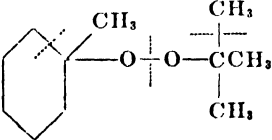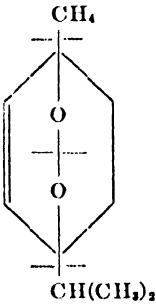
NO.	PEROXIDE	CONDITIONS	PRODUCTS	REFERENCE
1...	$(C_2H_5)_3COOC(C_2H_5)_3$	250°C., glass wool	$C_2H_5COC_2H_5 + n\text{-}C_4H_{10}$	(46)
2...		250°C., glass wool	$CH_3COCH_3 + (CH_3)_4C$	(46)
3...		250°C., glass wool	$C_2H_6 + CH_3COCH_3 +$ $CH_3(CH_2)_3CHCOCH_3 +$ $\quad\quad\quad\quad\ \ CH_3$ $CH_3(CH_2)_3CHCOCH_3$ $\quad\quad\quad\quad CH_3(CH_2)_3CHCOCH_3$	(46)
4...		Distil in nitrogen	$C_2H_6 + C_3H_6 +$ $\quad CH_3CH{=}CH_2$	(40)
5...		H_2O, 120–130°C.	$C_6H_5COC_6H_5 + HCHO$	(60)
6...		Vapor	$CH_3COCH_3 + C_2H_6$	(33)
7...		Boiling xylene	$(C_6H_5)_2COC_6H_5$ $\quad\quad\ \ |$ $(C_6H_5)_2COC_6H_5$	(71)

TABLE 1—*Concluded*

NO.	PEROXIDE	CONDITIONS	PRODUCTS	REFERENCE
8...	$CH_3CH_2CH_2O$ — $CH_3CH_2CH_2O$	230°C.	$CH_3CH_2CH_2CH_3 + HCHO$	(34)
9...	Mes—CH—C(H)—C(OH)—Mes* ; C₆H₅, O——O	Melt	Mes—C(C₆H₅)=CHOH + MesCOOH	(31)
10...	$(C_6H_5)_2CHC$—C(H)(OH)—C—Mes* ; O——O	Melt	$(C_6H_5)_2CHCHO$ + MesCOOH	(44)
11...	$(Mes)_2CHC$—C(H)(OH)—C—Mes* ; O——O	Melt	$(Mes)_2C=CHOH$ + MesCOOH	(31)
12...	p-ClC₆H₄CH—C(H)(OH)—C—Mes* ; Mes O——O	Melt	p-ClC₆H₄C(Mes)=CHOH	(31)

* Mes = H₃C—C₆H₃(CH₃)— .

An interesting application and an unusual example of the peroxide cleavage reaction has been reported by Criegee (16):
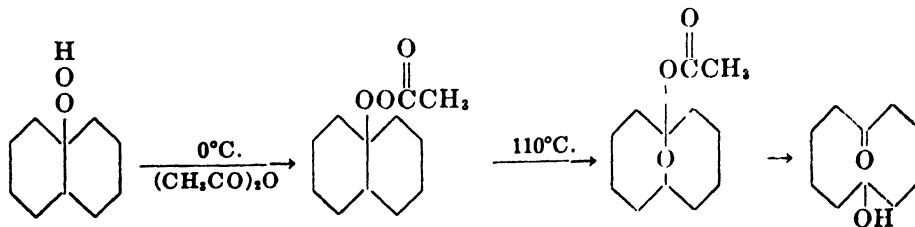
This is analogous to the rearrangement of triphenylmethyl peroxide.

Another variation is the decomposition of ketene peroxides, for example (62):

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup C{=}C{=}O \\ C_6H_5 \end{array} \xrightarrow{O_2} \left(\begin{array}{c} CH_3 \\ | \\ -O-C-\!\!-C-O- \\ | \quad \| \\ C_6H_5 \; O \end{array} \right)_n \rightarrow C_6H_5COCH_3 + CO_2$$
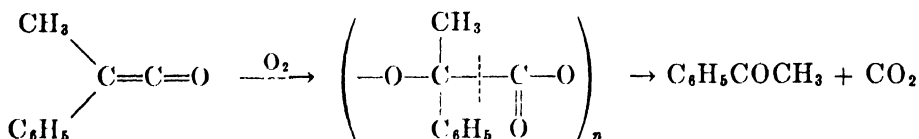
C. Hydroperoxides

Like the dialkyl peroxides, the hydroperoxides tend to cleave at the α-carbon atom. A few such reactions are summarized in table 2. The course of the reactions numbered 3, 4, and 5 may not be immediately obvious, on account of the further

TABLE 2

Decomposition of alkyl hydroperoxides

NO.	PEROXIDE	CONDITIONS	PERTINENT PRODUCTS	REFERENCE
1.	CH_3CH_2OOH	Sealed tube, 100°C.	HCHO	(34)
2.	$C_6H_5C{-}O{-}{-}OH$ with C_6H_5 above and C_6H_5 below	Melt	$C_6H_5COC_6H_5 +$ C_6H_5OH	(72)
3.	OOH (cyclohexene ring)	Dilute H_2SO_4	(ring)CHO	(25, 38)
4.	OOH (ring with CH_3)	Dilute H_2SO_4	(ring)COCH_3	(25)
5.	OOH (ring with CH_3, CH_3)	Dilute H_2SO_4	(ring)CH_3 COCH_3	(25)
6.	$(CH_3)_3COOH$	Vapor phase	CH_3COCH_3	(33)
7.	$CH_3CH_2CH_2OOH$	Glass wool, heat	$CH_3CH_3 + HCHO$	(34)

TABLE 3

The reactions of carbonium ions with hydrogen peroxide
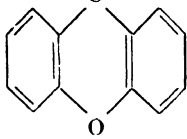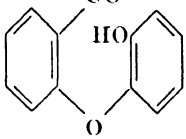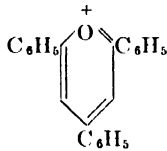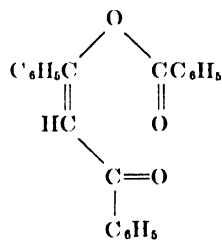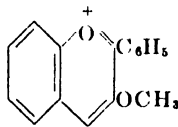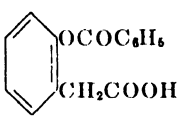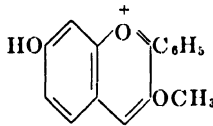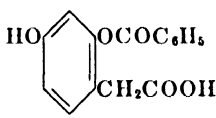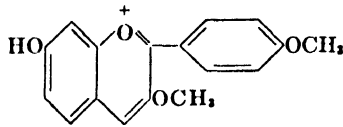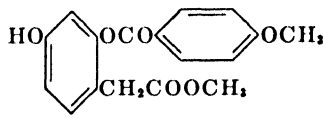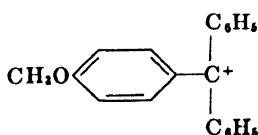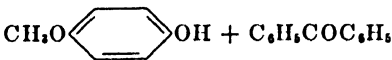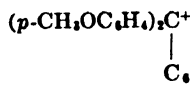
NO.	CARBONIUM ION	PRODUCT	REFERENCE
1...	C_6H_5 — xanthylium cation (C$^+$ with two fused benzene rings bridged by O)	C_6H_5 — CO ; HO ; diphenyl ether carbonyl product (O bridge)	(54)
2...	C_6H_5 — O$^+$ — C_6H_5 with C_6H_5 (triphenylpyrylium)	C_6H_5C—O—CC_6H_5 ; HC ; O ; C=O ; C_6H_5	(22)
3...	O$^+$—C_6H_5 ; OCH$_3$ (benzopyrylium)	OCOC$_6$H$_5$; CH$_2$COOH	(20)
4...	HO— O$^+$—C_6H_5 ; OCH$_3$	HO— OCOC$_6$H$_5$; CH$_2$COOH	(20)
5...	HO— O$^+$—C_6H_5—OCH$_3$; OCH$_3$ (picrate)	HO— OCO— —OCH$_3$; CH$_2$COOCH$_3$	(20)
6...	CH_3O— —C^+ with C_6H_5 and C_6H_5	CH_3O— —OH + $C_6H_5COC_6H_5$	(23)
7...	$(p\text{-}CH_3OC_6H_4)_2C^+$; C_6H_5	$p\text{-}CH_3OC_6H_4OH$ + $p\text{-}CH_3OC_6H_4COC_6H_5$	(23)

TABLE 3—*Concluded*

NO.	CARBONIUM ION	PRODUCT	REFER-ENCE
8...	$(p\text{-}CH_3OC_6H_4)_3C^+$	$p\text{-}CH_3OC_6H_4OH +$ $(p\text{-}CH_3OC_6H_4)_2CO$	(23)
9...	$(p\text{-}C_6H_5OC_6H_4)_2C^+$ $\vert$ C_6H_5	$p\text{-}C_6H_5OC_6H_4COC_6H_5 +$ $p\text{-}C_6H_5OC_6H_4OH$	(23)
10...	$(p\text{-}C_6H_5OC_6H_4)_3C^+$	$(p\text{-}C_6H_5OC_6H_4)_2CO +$ $p\text{-}C_6H_5OC_6H_4OH$	(23)
11...	$(p\text{-}O_2NC_6H_4)_3C^+$	$(p\text{-}O_2NC_6H_4)_2CO +$ $p\text{-}O_2NC_6H_4OH$	(23)
12...	$p\text{-}O_2NC_6H_4\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{C^+}}$	$p\text{-}O_2NC_6H_4COC_6H_5 + C_6H_5OH$	(23)

changes that follow the initial cleavage. The products can be accounted for as follows:
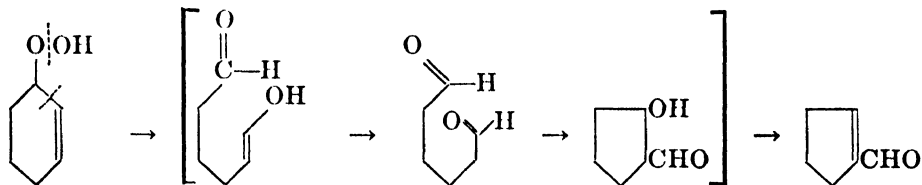
Adipic dialdehyde was isolated in some experiments.
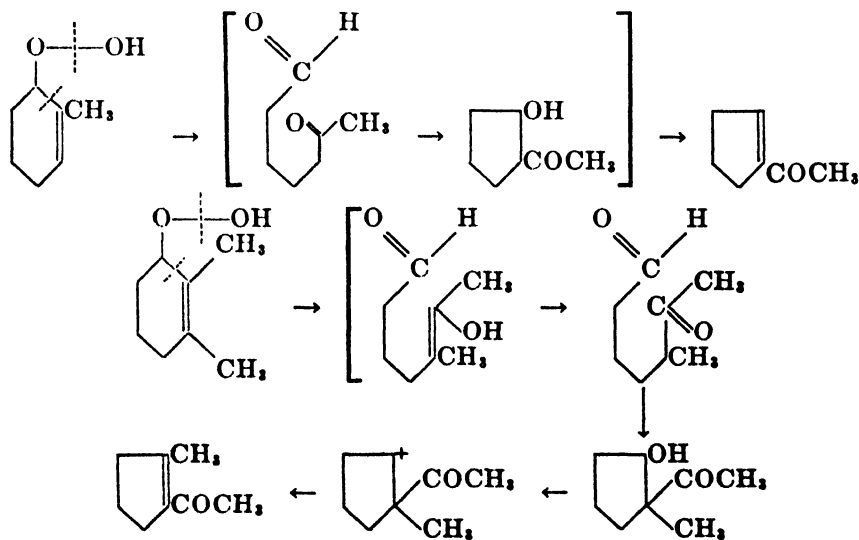
The reactions of carbonium ions with hydrogen peroxide can best be explained as hydroperoxide decompositions. Dilthey and his collaborators have in fact isolated hydroperoxides from carbonium ions in six cases. But usually the product isolated from the reaction of a carbonium ion with hydrogen peroxide is that to be expected from the decomposition of the hydroperoxide, rather than the hydroperoxide itself. A number of such reactions are given in table 3. Let us consider reaction 2 of table 3 as an example:
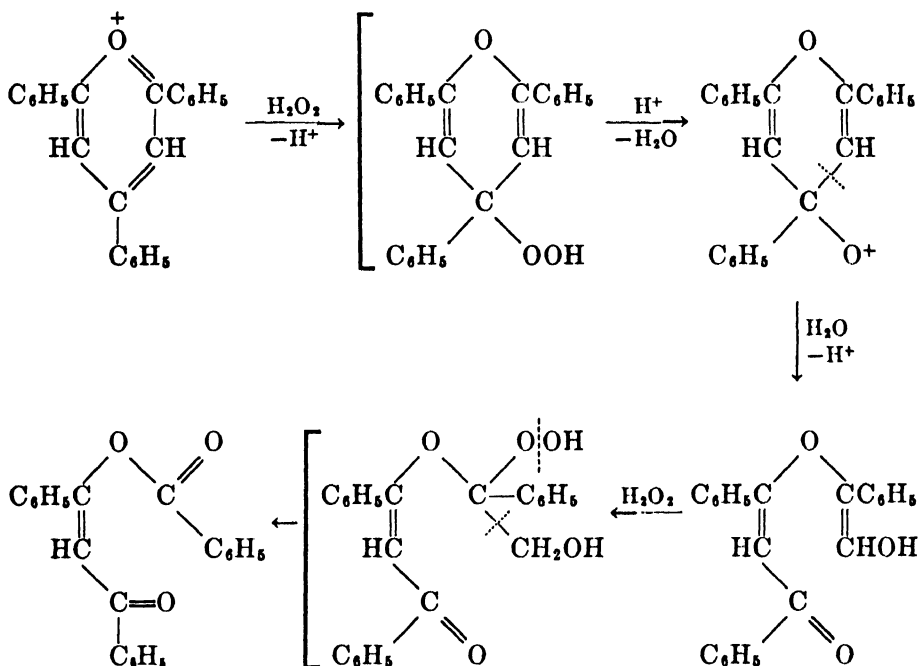
The other reactions listed involve fewer steps.

It will be seen from the reactions of table 3 that the effect of substituents on the course of the reaction favors the oxygen cation interpretation rather than the oxygen radical one. Some of the autoxidations with hydroperoxide intermediates, to be described later, however, follow a course that suggests free-radical intermediates. The present author has made some attempts (unpublished) to induce ionic decomposition of tertiary butyl hydroperoxide with acids; the only effect of acids was to reverse the addition of hydrogen peroxide to isobutylene by which tertiary butyl hydroperoxide is formed. Wieland and Maier report (72) that triphenylmethyl hydroperoxide is stable in acids; the decomposition induced by heat alone is therefore a radical reaction. Acids should catalyze the ionic reaction by the following mechanism:

$$\text{ROOH} + \text{H}^+ \longrightarrow \overset{\text{H}}{\underset{.}{\text{ROOH}}} \rightarrow \text{RO}^+ + \text{H}_2\text{O}$$

Wieland and Maier (72) also report that triphenylmethyl peroxide reacts readily with benzoyl chloride to form:

$$C_6H_5COOC(C_6H_5)_2$$
$$\underset{OC_6H_5}{|}$$
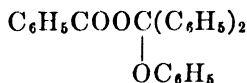
This probably goes by way of the perester.

D. Autoxidation

Hydroperoxides are sometimes isolated from hydrocarbons exposed to air (25, 38). This, together with the correspondence between the products of autoxidation and the products of hydroperoxide decomposition, makes it seem likely that hydroperoxides are intermediate in the autoxidation reaction (70). A number of reactions susceptible to such an interpretation are listed in table 4. The hydroperoxide is commonly formed at a tertiary carbon or at a carbon atom in the α-position to a double bond. Reaction 1 would thus be formulated as follows:
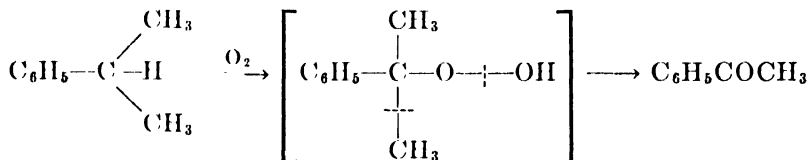
On the other hand, reaction 3 probably goes by removal of a hydrogen atom to give an alkoxy free radical.

Reaction 8 (of table 4) is more complicated than some of the others. The following hydroperoxide intermediate satisfies both the preference for a tertiary carbon atom and an allylic double bond:
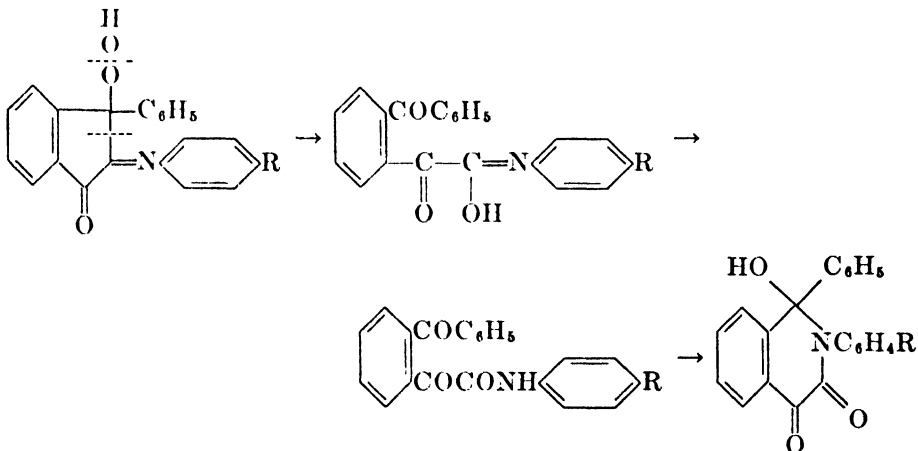
In table 4 there are also listed autoxidations of another kind, in which oxygen is added to a double bond or system of double bonds. Reaction 15, which goes by way of a ketene peroxide, is of this type. The ketene peroxides are very unstable but are sometimes isolated (62).

TABLE 4

Cleavage during autoxidation
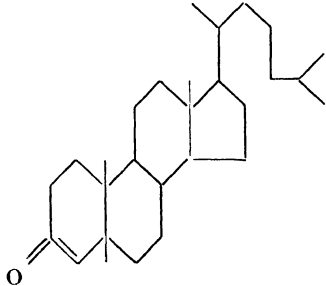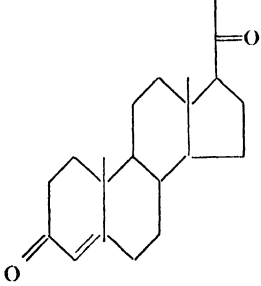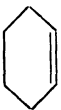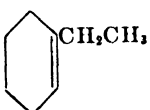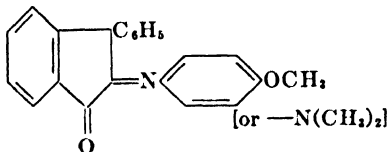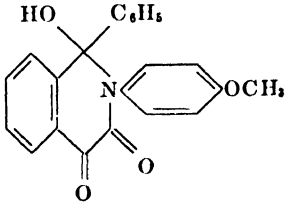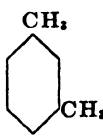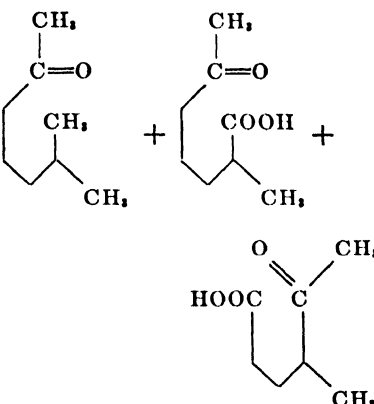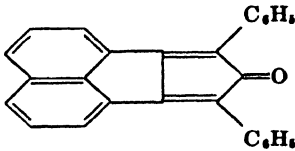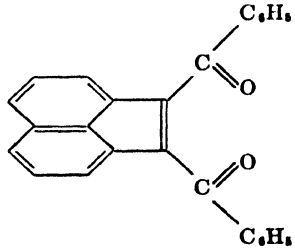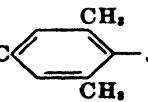
NO.	SUBSTANCE	PRODUCT	REFER-ENCE
1...	$C_6H_5CH(CH_3)_2$	$C_6H_5COCH_3$	(63)
2...	p-$CH_3C_6H_4CH(CH_3)_2$	p-$CH_3C_6H_4COCH_3$	(63)
3...	$\begin{matrix} CH_3 \\ \| \\ C_6H_5COH \\ \| \\ CH_3 \end{matrix}$	$C_6H_5COCH_3$ (trace)	(64)
4...	$\begin{matrix} H \\ \| \\ C_6H_5CC_2H_5 \\ \| \\ OH \end{matrix}$	C_6H_5CHO (trace)	(64)
5...			(10)
6...		CHO	(51)
7...	CH_2CH_3	$COCH_2CH_3$	(51)
8...			(53)
9...	$\begin{matrix} CH_3 \quad OH^* \\ \| \qquad \| \\ Mes-C=C \\ \qquad\quad \| \\ \qquad\quad Mes \end{matrix}$	$MesCOCH_3 + MesOH + CO$	(29)

TABLE 4—*Continued*

NO.	SUBSTANCE	PRODUCT	REFER-ENCE
10...	(structure) CH₃ / OH * Mes—C=C with H₃C, CH₃ / H₃C, CH₃ aromatic ring	$MesCOCH_3 + CO +$ (structure: H₃C CH₃ / OH / H₃C CH₃)	(29)
11...	(structure) CH₃ OH Mes—C=C CH₃ * / Br / H₃C, CH₃	$MesCOCH_3 +$ (structure: CH₃ / HO Br / H₃C CH₃)	(30)
12 .	(structure) CH₃ Mes * CH₃ C=C Br / OH / H₃C CH₃	(structure: CH₃ / Br COCH₃ / H₃C CH₃) $+ MesOH$	(30)
13...	Mes—CCH₃—CH₃C—Mes * / C C / Mes OH HO Mes	$MesOH + MesCOCH_2CH_3COMes$	(28)
14...	(structure) CH₃ C=C=O C₆H₅	$CH_3COC_6H_5 + CO_2$	(62)
15...	$(C_6H_5)_2C=C=O$	$C_6H_5COC_6H_5 + CO_2$	(62)
16...	(structure) CH₃ ring CH₃	(structure: CH₃ / O=C / CH₃ / CH₃CH₃CHCH₃) $+$ (structure: COOH CH₂COCH₃ / CH₃—CH / CH₃)	(12)

TABLE 4—*Concluded*

NO.	SUBSTANCE	PRODUCT	REFERENCE
17...	CH₃ ... CH₃		(13)
18...	H C₆H₅CCH₃ R (R = ethyl, *n*-propyl, or *n*-butyl)	C₆H₅COCH₃	(65)
19...	(C₆H₅)₃CH	C₆H₅COC₆H₅ + C₆H₅OH	(65)
20...	CH₃ C₆H₅CH C₆H₅	C₆H₅COC₆H₅ + HCOOH	(65)
21...	Mes * Mes—C—Cl + Ag H	MesOH + MesCOOH + (Mes)₂CO	(49)
22...		+ CO	(19)

Note: For readability the structural drawings in rows 17 and 22 are rendered as images.

* Mes = H₃C— (2,4,6-trimethylphenyl with CH₃ groups) —.

$$\left[\begin{array}{c} C_6H_5 \quad O \\ \| \\ -O-C---C-O^- \\ | \\ C_6H_5 \end{array}\right]_n \longrightarrow (C_6H_5)_2CO + CO_2$$

Similarly, reaction 22 may go by way of a 1,4-adduct:

The autoxidation of enols (reactions 9–13) could be formulated in either of two ways:

$$(a) \qquad \underset{Mes-C=C-Mes}{\overset{H_3C \quad OH}{}} + O_2 \longrightarrow \left[\underset{Mes-C---C-Mes}{\overset{H_3C \quad OH}{\underset{O---O}{}}}\right]$$

or

$$(b) \qquad \underset{Mes-C=C-Mes}{\overset{H_3C \quad OH}{}} \rightleftharpoons \underset{Mes-C-C-Mes}{\overset{CH_3}{\underset{H \quad O}{}}}$$

$$\downarrow$$

$$\left[\underset{Mes-C-C-Mes}{\overset{CH_3}{\underset{O \quad O}{\underset{O}{\underset{H}{}}}}}\right]$$

Path (b) is greatly to be preferred for reactions 9–13. Although it is true that peroxides like that of path (a) have been made by the air oxidation of enols (see reaction 9 of table 1), such peroxides decompose to carboxylic acids. This is to be expected, since the carbon atom of the future carboxyl group already bears a hydroxyl and formation of the carboxylic acid is a one-step process. But in reactions 9–13 of table 4 the product is not a carboxylic acid, but carbon monoxide and a phenol. Such a result is readily explained by path (b), since acyl radicals are known to lose carbon monoxide.

$$\text{Mes}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{H}{|}}{\overset{|}{O}}}{C}}-\overset{\overset{\displaystyle O}{\parallel}}{C}-\text{Mes} \longrightarrow HO\cdot + \text{Mes}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\cdot}{\overset{|}{O}}}{C}}-\overset{\overset{\displaystyle O}{\parallel}}{C}-\text{Mes}$$

$$\downarrow$$

$$\text{Mes}-\overset{\overset{\displaystyle }{}}{\underset{\underset{O}{\parallel}}{C}}-CH_3 + \text{Mes}\overset{\overset{\displaystyle O}{\parallel}}{C}\cdot$$

$$\overset{\overset{\displaystyle O}{\parallel}}{\text{Mes}C}\cdot + HO\cdot \longrightarrow \text{MesOH} + CO$$

Although some intermediate hydroperoxides decompose by way of oxygen cations (see page 393), it will be seen by inspection of table 4 that the order of bond cleavage in autoxidation often indicates an oxygen free-radical mechanism for the decomposition of the hydroperoxide. For example, in reactions 1, 2, 5, 18, and 20 of table 4, it is the alkyl group that is split off rather than the aryl group.

Whether the decomposition of a given hydroperoxide involves radical or cationic intermediates probably depends on the amount of polarization of the peroxide bond by the other groups attached to the perhydroxylated carbon atom.

Those reactions of table 3 whose products are those to be expected on the basis of an ionic mechanism all involve compounds containing groups which place a partial negative charge on the alpha carbon atom.

E. Ozonization

The ozonization of double bonds probably involves the preliminary formation of a "molozonide" (61). But the isolable ozonides appear to have a rearranged, "isozonide" structure. The most plausible mechanism is an ionic one:

$$R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\underset{O^-}{|}}{\overset{|}{O}}}{C}}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{}{\overset{|}{O^+}}}{C}}-R \longrightarrow R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{}{\overset{|}{O^+}}}{C}}-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\underline{O}}{|}}{\overset{|}{O}}}-R$$

$$\downarrow$$

$$\underset{R}{\overset{R}{>}}\overset{O}{\underset{\underset{O}{|}}{C}}\overset{}{\underset{O}{\diagup}}C\overset{<R}{<R} \longleftarrow \underset{R}{\overset{R}{>}}\overset{}{\underset{+}{C}}-O-\overset{}{\underset{\underset{\underline{O}}{|}}{C}}\overset{<R}{<R}$$
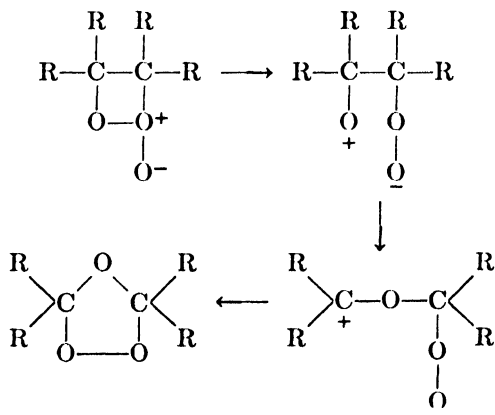
Support for the ionic mechanism, aside from the inherent plausibility of ionic cleavage of a bond that bears a polar group on one end, is derived from the occasionally abnormal course of ozonization. When one of the carbon atoms next

to the double bond bears an oxygen or nitrogen atom (an electron-donating atom) or when it is part of a benzene ring bearing the sort of substituent that encourages migration within a carbonium ion, oxygen is introduced between the double bond and the carbon atom in question (35, 36, 52, 58, 75). The more electron-donating the substituent, the greater is the proportion of abnormal product. Table 5 contains typical examples of abnormal ozonolysis. All of these deviations from the usual path of ozonolysis can be explained by the mechanism below, in which R is a group of the type suited to migration within a carbonium ion.

$$-\overset{|}{C}=\overset{|}{C}-R \quad \underset{\underset{\overset{-O}{|}}{\overset{+O-O}{|}}}{O=\overset{+}{O}-\overset{-}{O}} \rightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R \longrightarrow -\overset{|}{\underset{O}{C}}-\overset{|}{\underset{\overset{O}{+}}{C}}-R$$

$$\downarrow$$

$$-\overset{|}{\underset{\overset{||}{O}}{C}} + \overset{|}{\underset{\overset{||}{O}}{C}}-OR \longleftarrow -\overset{|}{\underset{\overset{O}{|}}{C}}\overset{|}{\underset{\overset{|}{O}}{C}}-OR \longleftarrow -\overset{|}{\underset{\overset{O}{|}}{C}}-\overset{|}{\underset{+}{C}}-O-R$$

$$\qquad I \qquad II \qquad\qquad\qquad\qquad \overset{O}{\underset{-}{}}$$
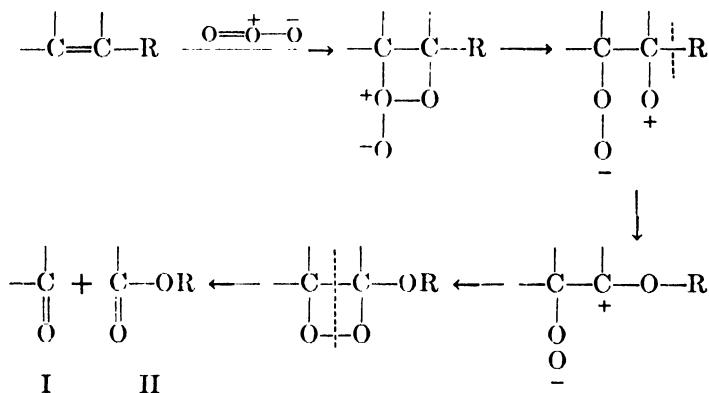
The fate of product II is observed to depend on details of its structure not shown. For example, if it is

$$\overset{H}{\underset{\overset{||}{O}}{\underset{|}{C}}}-O-\overset{R}{\underset{\overset{|}{OR}}{\underset{|}{C}}}-H$$
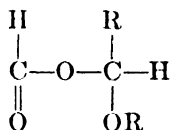
it will lose carbon monoxide as the ozonide decomposes. Young *et al.* (75) report that carbon monoxide is evolved spontaneously from the ozonide even below room temperature; this is further evidence of an unusual structure.

As will be seen in the next section of this review, carbonyl compounds are also attacked by ozone and by hydrogen peroxide. Accordingly, if the reaction mixture is wet during the ozonization, part of the abnormal product may come from attack by ozone or by hydrogen peroxide on the hydrolysis products of the normal ozonide. Evidence that the latter is not the principal explanation of abnormal ozonolyses is provided, however, by the isolation of abnormal ozonides (75). Furthermore, the yields of phenols from aldehydes are lower than the yields of phenols from the corresponding cinnamic esters under comparable conditions (58). Hydrogenation rather than hydrolysis of the ozonide does not prevent the formation of abnormal products (69, 75).

III. REACTIONS BETWEEN PEROXIDES AND CARBONYL COMPOUNDS

A. Ozone

In table 6 are gathered some examples of the ozonolysis of carbonyl compounds. Large-ring ketones are ozonized to the corresponding dicarboxylic acids in good

TABLE 5

Abnormal ozonizations
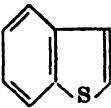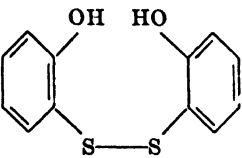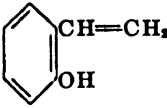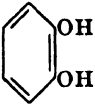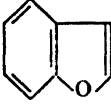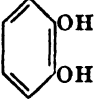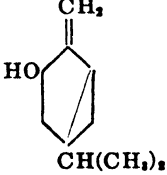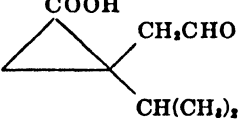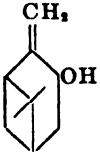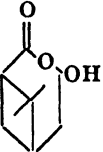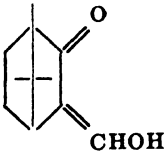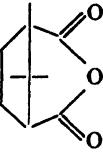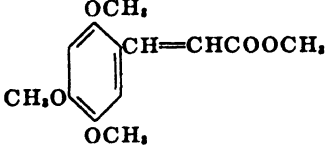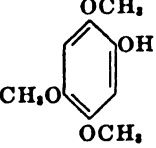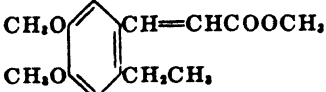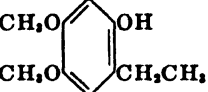
NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD	REFERENCE
			per cent	
1...				(69)
2...			10	(69)
3...			10	(69)
4...				(35)
5...				(36)
6...				(52)
7...			48.2	(58)
8...			46.4	(58)

TABLE 5—*Continued*
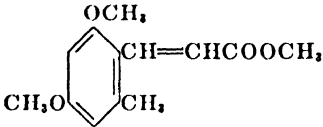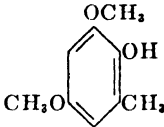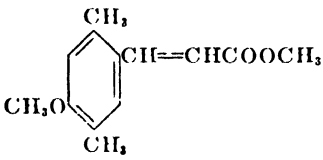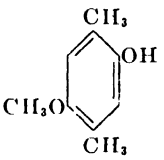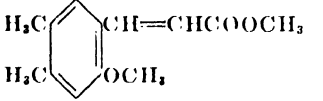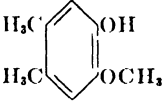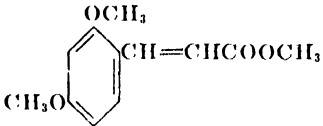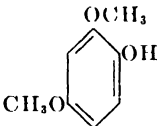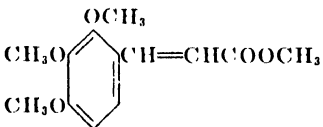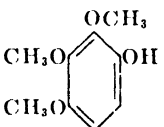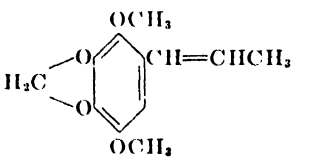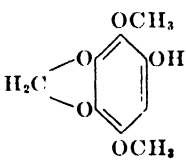
NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD	REFERENCE
			per cent	
9...			27.1	(58)
10...			22.0	(58)
11...			15.9	(58)
12...			15.0	(58)
13...			13.7	(58)
14...			5	(58)
15...	$CH_3CH{=}CHCH_2OC_6H_4NO_2(p)$	HCOOH	8*	(75)
16..	$CH_3CH{=}CHCH_2OC_6H_5$	HCOOH	15*	(75)
17...	$CH_3CH{=}CHCH_2OH$	HCOOH	23*	(75)
18...	$CH_3CHOHCH{=}CH_2$	CH_3COOH	25*	(75)
19...	$CH_3(CH_2)_3CHOHCH{=}CH_2$	$CH_3(CH_2)_3COOH$	38*	(75)
20...	$CH_3(CH_2)_2CHOHCH{=}CHCH_3$	$CH_3(CH_2)_2COOH$	50*	(75)
21...	$CH_3CH_2CHOHCH{=}CHCH_3$	CH_3CH_2COOH	15*	(75)
22...	$C_6H_5CH{=}CHCH_2OH$	HCOOH	60*	(75)

TABLE 5—*Concluded*

NO.	SUBSTRATE	ABNORMAL PRODUCT	YIELD	REFER-ENCE
			per cent	
23...	$CH_3CH=CHCH_2OCH_2CH_3$	HCOOH	25*	(75)
24...	$CH_3CH_2O\overset{\overset{\displaystyle CH_3}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}}CH=CH_2$	CH_3COOH	35*	(75)
25...	$CH_3CH=CHCH_2N(C_2H_5)_2$	HCOOH	54*	(75)
26...	$CH_3CH=CHCOOH$	HCOOH	5*	(75)
27...	$CH_3CH=CHCHO$	HCOOH	10*	(75)
28..	$CH_3CH=CHCOCH_2CH_3$	HCOOH	13*	(75)

* Per cent of total acids after treatment with silver oxide.

yield and without undesirable byproducts (66). A mechanism for the reaction with carbonyl compounds might be:

$$\underset{\displaystyle R\overset{\displaystyle O}{\overset{\|}{C}}R'}{} + O=O-O \rightarrow \left[R-\overset{\overset{\displaystyle \bar{O}}{|}}{\underset{\underset{\displaystyle O}{\|}}{\underset{O^+}{C}}}-R' \right] \longrightarrow RCOOR' + O_2$$

$$\longrightarrow RCOO^- + R^+ + O_2$$

$$R^+ + O_3 \rightarrow RCH_2O^+ + O_2$$

$$\downarrow$$

$$RCHO + H^+ \rightarrow RCOOH$$
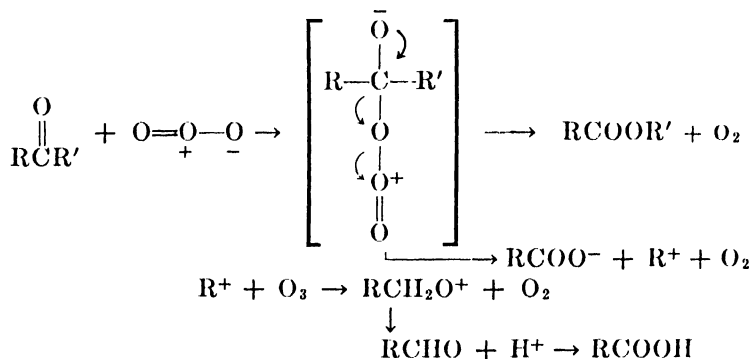
An aldehyde (R or R' is hydrogen) can give either an acid or an ester of formic acid, depending on whether the hydrogen or the other group migrates. Ordinarily, the hydrogen migrates and the product is an acid. But when the alkyl or aryl group is of the sort that migrates within a carbonium ion, a certain amount of phenol or other degraded product is formed. The phenol is produced by way of the formate. Acids, but not the likewise expected esters, are formed with ketones.

A methoxyl group in the meta position does not lead to phenol formation when benzaldehydes are ozonized (68).

B. *Hydroperoxides*

A number of reagents other than ozone oxidize aldehydes and ketones to the corresponding esters or lactones. Such reagents have in common the perhydroxyl group. Table 7 lists some oxidations of this type; in each case the reagent is hydrogen peroxide, Caro's acid (monopersulfuric acid), peracetic acid, perbenzoic
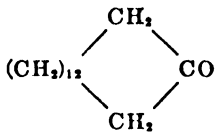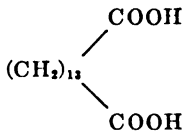
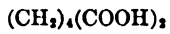## TABLE 6

Ozonolysis of carbonyl compounds
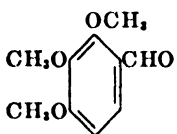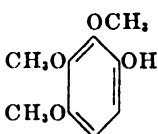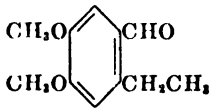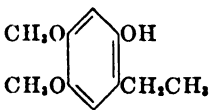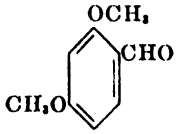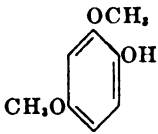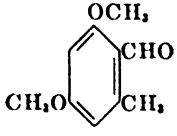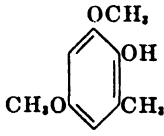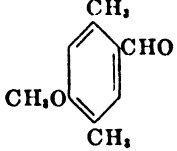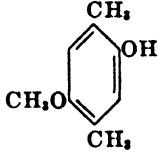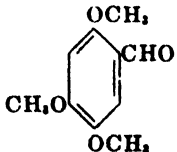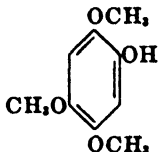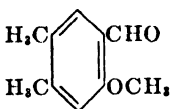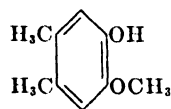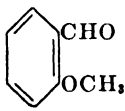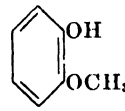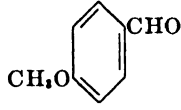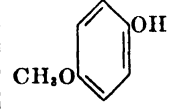
NO.	SUBSTRATE	PRODUCT	YIELD	REFERENCE
			per cent	
1...	$(CH_2)_{12}$ with CH_2—CO—CH_2 ring	$(CH_2)_{13}$ with $COOH$ and $COOH$		(66)
2...	cyclohexanone (ring with O)	$(CH_2)_4(COOH)_2$		(66)
3...	OCH_3 / CH_3O—ring—CHO / CH_3O	OCH_3 / CH_3O—ring—OH / CH_3O	20.1	(58)
4...	CH_3O—ring—CHO / CH_3O—CH_2CH_3	CH_3O—ring—OH / CH_3O—CH_2CH_3	14.5	(58)
5...	OCH_3 / ring—CHO / CH_3O	OCH_3 / ring—OH / CH_3O	14.0	(58)
6...	OCH_3 / ring—CHO / CH_3O—CH_3	OCH_3 / ring—OH / CH_3O—CH_3	8.0	(58)
7...	CH_3 / ring—CHO / CH_3O—CH_3	CH_3 / ring—OH / CH_3O—CH_3	4.4	(58)
8...	OCH_3 / ring—CHO / CH_3O—OCH_3	OCH_3 / ring—OH / CH_3O—OCH_3	4.1	(58)

TABLE 6—*Concluded*

NO.	SUBSTRATE	PRODUCT	YIELD	REFER-ENCE
			per cent	
9...	H_3C—[benzene ring]—CHO, H_3C—OCH$_3$	H_3C—[benzene ring]—OH, H_3C—OCH$_3$	3.9	(58)
10...	[benzene ring]—CHO, OCH$_3$	[benzene ring]—OH, OCH$_3$	3	(68)
11...	[benzene ring]—CHO, CH_3O—	[benzene ring]—OH, CH_3O—	4	(68)

acid, or perphthalic acid. The reagent, ROOH, evidently adds to the carbonyl double bond:

405
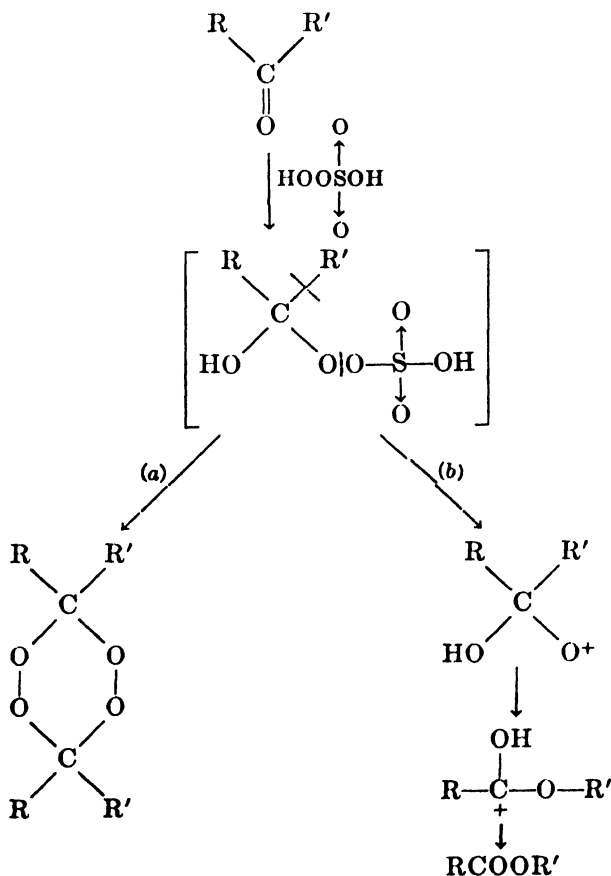
TABLE 7

Reactions of carbonyl compounds with hydroperoxides

NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
1...	(benzene ring with OCH₃, CHO, CH₃O substituents)	H₂O₂ in ether	(benzene ring with OCH₃, OH, CH₃O substituents)	(59)
2...	(benzene ring with OCH₃, CHO, CH₃O, OCH₃ substituents)	H₂O₂ in ether	(benzene ring with OCH₃, OH, CH₃O, OCH₃ substituents)	(59)
3...	(benzene ring with CH₃O, CHO, CH₃O, CH₂CH₃ substituents)	H₂O₂ in ether	(benzene ring with CH₃O, OH, CH₃O, CH₂CH₃ substituents)	(59)
4...	(benzene ring with CHO, CH₃O substituents)	H₂O₂ in ether	(benzene ring with OH, CH₃O substituents)	(59)
5...	(benzene ring with CHO, OCH₃ substituents)	H₂O₂ in ether	(benzene ring with OH, OCH₃ substituents)	(59)
6...	(benzene ring with CHO, CH₃O, OCH₃ substituents)	H₂O₂ in ether	(benzene ring with OH, CH₃O, OCH₃ substituents)	(59)
7...	(benzene ring with CHO)	H₂O₂ in ether	(benzene ring with OH) (only 0.7 per cent)	(59)
8...	$(CH_2)_{12}$ ring with CH₂, CH₂, C=O	H_2O_2, H_2SO_4	$(CH_2)_{13}$ ring with CH₂, O, CO	(66)
9...	$(CH_2)_{12}$ ring with CH₂, CH₂, C=O	HOOSO₃H, CH₃COOH	$(CH_2)_{13}$ ring with CH₂, O, CO	(56)

TABLE 7—Continued

NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFER-ENCE
10...	$(CH_2)_{10}$ ring with CH_2 / CH_2 and $C=O$	$HOOSO_3H$, CH_3COOH	$(CH_2)_{11}$ ring with CH_2, O, CO	(56)
11...	$(CH_2)_{11}$ ring with CH_2 / CH_2 and $C=O$	$HOOSO_3H$, CH_3COOH	$(CH_2)_{12}$ ring with CH_2, O, CO	(56)
12...	$(CH_2)_{13}$ ring with CH_2 / CH_2 and $C=O$	$HOOSO_3H$, CH_3COOH	$(CH_2)_{14}$ ring with CH_2, O, CO	(56)
13...	$(CH_2)_{14}$ ring with CH_2 / CH_2 and $C=O$	$HOOSO_3H$, CH_3COOH	$(CH_2)_{15}$ ring with CH_2, O, CO	(56)
14...	$C_6H_5COC_6H_5$	H_2O_2, H_2SO_4	$C_6H_5COOC_6H_5$	(21)
15...	cyclohexanone with CH_3 (top) and $CH(CH_3)_2$ (bottom), $=O$	H_2O_2, H_2SO_4	lactone with CH_3 (top), O, $=O$, $CH(CH_3)_2$ (bottom)	(21)
16...	cyclohexanone with CH_3 (top) and $CH(CH_3)_2$ (bottom), $=O$	$HOOSO_3H$	lactone with CH_3 (top), O, $=O$, $CH(CH_3)_2$ (bottom)	(3)
17...	$(CH_2)_4$ ring with CH_2 / CH_2 and $C=O$	$HOOSO_3H$	$(CH_2)_5$ ring with CH_2, O, CO	(3)
18...	cyclohexanone with CH_3 (top) and $CH(CH_3)_2$ (bottom), $=O$	$HOOSO_3H$	lactone with CH_3, O, $C=O$, $CH(CH_3)_2$ (bottom)	(2)

TABLE 7—*Continued*
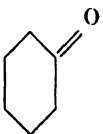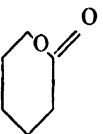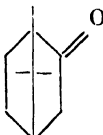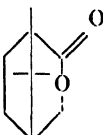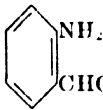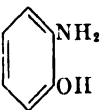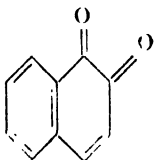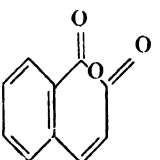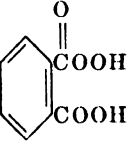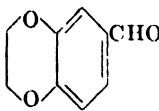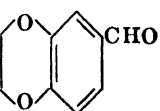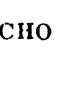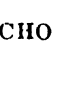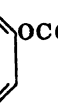
NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFER-ENCE
19 ..		$HOOSO_3H$		(2)
20 ..		$HOOSO_3H$		(2)
21..	NH₂ / CHO	$HOOSO_3H$	NH$_2$ / OH	(4)
22 .		C_6H_5COOH / O		(42)
23 .	$C_6H_5(CH=CH)_2CO$ $\mid$ $C_6H_5(CH=CH)_2CO$	COOH / COOH	$C_6H_5(CH=CH)_2CO$ O $C_6H_5(CH=CH)_2CO$	(41)
24	CHO	$CH_3\overset{O}{C}OOH,$ $CH_3COOH,$ H$^+$	$HCOOH +$ CHO	(7)
25...	CH_3O CHO CH_3O	$CH_3\overset{O}{C}OOH,$ trace of $p\text{-}CH_3C_6H_4SO_3H$	CH_3O $OCOCH_3 +$ $HCOOH$ CH_3O	(8)
26...	CH_3O CHO C_2H_5O	$CH_3\overset{O}{C}OOH,$ trace of $p\text{-}CH_3C_6H_4SO_3H$	CH_3O $OCOCH_3 +$ $HCOOH$ C_2H_5O	(8)

TABLE 7—*Continued*

NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFER-ENCE
27...	$C_2H_5O-C_6H_3(CH_3O)-CHO$	$CH_3\overset{O}{\overset{\|}{C}}OOH$, trace of $p\text{-}CH_3C_6H_4SO_3H$	$C_2H_5O-C_6H_3(CH_3O)-OCOCH_3 + HCOOH$	(8)
28...	$C_2H_5O-C_6H_3(C_2H_5O)-CHO$	$CH_3\overset{O}{\overset{\|}{C}}OOH$, trace of $p\text{-}CH_3C_6H_4SO_3H$	$C_2H_5O-C_6H_3(C_2H_5O)-OCOCH_3 + HCOOH$	**(8)**
29...	$CH_3O-C_6H_3(n\text{-}C_4H_9O)-CHO$	$CH_3\overset{O}{\overset{\|}{C}}OOH$, trace of $p\text{-}CH_3C_6H_4SO_3H$	$CH_3O-C_6H_3(n\text{-}C_4H_9O)-OCOCH_3 + HCOOH$	(8)
30...	$C_6H_4(CHO)(OH)$	H_2O_2, CH_3COOH	$C_6H_4(OH)(OH)$	(69)
31...	$(p\text{-}O_2NC_6H_4)_2CO$	H_2O_2, H_2SO_4	$p\text{-}O_2NC_6H_4COOH + p\text{-}O_2NC_6H_4OH$	(23)
32...	$p\text{-}O_2NC_6H_4COC_6H_5$	H_2O_2, H_2SO_4	$p\text{-}O_2NC_6H_4COOH + C_6H_5OH$	(23)
33...	$C_6H_4(CHO)(OH)$	H_2O_2, NH_3	$C_6H_4(OH)(OH)$	(17)
34...	$C_6H_4(CHO)(HO)$	H_2O_2, NH_3	$C_6H_4(OH)(HO)$	(17)
35...	$C_6H_4(COCH_3)(OH)$	H_2O_2, NH_3	$C_6H_4(OH)(OH)$	(17)
36...	$C_6H_4(COCH_3)(HO)$	H_2O_2, NH_3	$C_6H_4(OH)(HO)$	(17)

TABLE 7—*Concluded*

NO.	CARBONYL COMPOUND	REAGENT	PRODUCT	REFERENCE
37	(benzene ring) OH, CHO, NO₂ — o-hydroxy-nitrobenzaldehyde	H_2O_2, NH_3	(benzene ring) OH, OH, NO₂	(17)
38	(benzene ring) CHO, HO, CH₃	H_2O_2, NH_3	(benzene ring) OH, HO, CH₃	(17)
39	(benzene ring) OH, COCH₃, CH₃O	H_2O_2, NH_3	(benzene ring) OH, OH, CH₃O	(17)
40	(benzene ring) CHO, OH	H_2O_2, (pyridine with N)	(benzene ring) OH, OH	(68)
41	(indoline ring) OCOCH₃, C₆H₅, N–COCH₃, =O	H_2O_2, OH^-	(benzene ring) COC₆H₅, NH₂	(39)
42	(indoline ring) OH, C₆H₄CH₃(p), N–H, =O	H_2O_2, OH^-	(benzene ring) COOH, H₃C	(39)
43	(indoline ring) OCOCH₃, C₆H₄CH₃(p), N–COCH₃, =O	H_2O_2, OH^-	(benzene ring) CO–(benzene ring)–CH₃, NH₂	(39)
44	C₆H₅CH=CHCOCH₃	CH₃COOH, O	C₆H₅CH=CHOCOCH₃	(9)
45	(bicyclic ketone with cyclopentane, C=O, O)	H_2O_2, CH₃COOH	(two cyclopentane rings) C–COOH, C–COOH, OH, OH	(45)

The various products can all be explained on the basis of the above scheme, except that the reactions of the α-diketones may involve cyclic intermediates.

Acetone reacts largely according to path (a), giving dimeric peroxide. Cyclic ketones, however, tend to react by path (b), giving lactones (3, 21, 56). Similarly, diketones give acid anhydrides (41, 42).

Support for the ionic mechanism is found in the observation of Dilthey et al. (21) that strong acid favors ester formation, while more dilute acid gives more of the dimeric peroxide. Acid apparently helps remove the sulfate ion in step (b).

The addition of hydroperoxides to carbonyl compounds can be catalyzed by either acid or base. In the former case a proton is added to the carbonyl oxygen; in the latter the attacking reagent is the anion of the hydroperoxide.

Reaction 45 of table 7, being more complicated than the others, deserves a little comment. It probably starts by addition of hydrogen peroxide and then involves a rearrangement accompanied by a displacement.
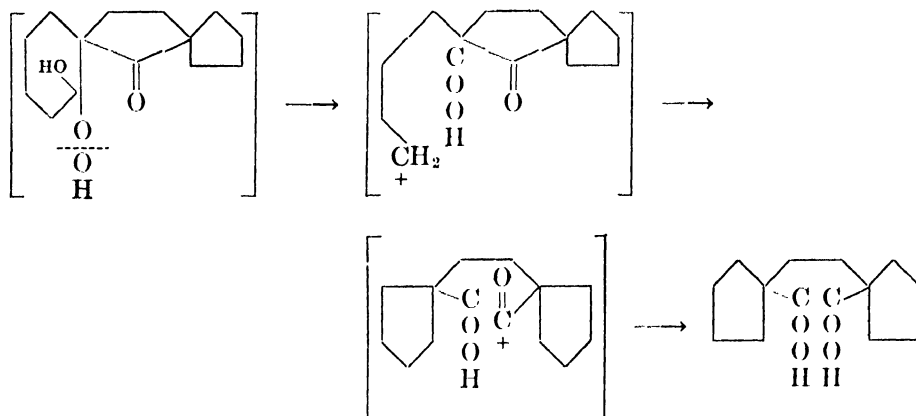
Aldehydes normally give carboxylic acids (scheme (b) of page 405; R' equals H). But when the group attached to the carbonyl is of the type likely to migrate in a carbonium ion, a certain amount of phenol, quinone (1), or (in the case of aliphatic aldehydes) degradation product is obtained. The nature of the groups favoring phenol formation (Dakin reaction) is such as to support the ionic mechanism; thus, vanillin gives the phenol while acetylvanillin gives only the acid (8). Scheme (b) of page 405 of course predicts not the phenol but the corresponding formate. In some cases the intermediate formates have been isolated (67).

Oleic acid ozonide has also been used as a reagent for the conversion of suitably substituted benzaldehydes to the corresponding phenols (69). Rieche (55) has shown that a decomposing ozonide gives some α-hydroxyhydroperoxide and that the latter can give up hydrogen peroxide to other carbonyl compounds. The mechanism of the oxidation with decomposing oleic acid ozonide need not then be different from that with the more usual reagents.

The mechanism proposed on page 405 is not the only one that can be written for the Dakin reaction. In 1903 Bamberger oxidized o-aminobenzaldehyde with Caro's acid to o-aminophenol. He isolated from the reaction mixture the N-formyl derivative of o-aminophenol, which led him to postulate the following reaction mechanism (4):

$$
\underset{\text{CHO}}{\overset{\text{NH}_2}{\bigcirc}} \xrightarrow{\text{HOOSO}_2\text{H}} \left[\underset{\text{CHO}}{\overset{\text{NHOH}}{\bigcirc}}\right] \longrightarrow
$$

$$
\underset{\text{OH}}{\overset{\text{NHCHO}}{\bigcirc}} \xrightarrow{\text{H}_2\text{O}} \underset{\text{OH}}{\overset{\text{NH}_2}{\bigcirc}} + \text{HCOOH}
$$
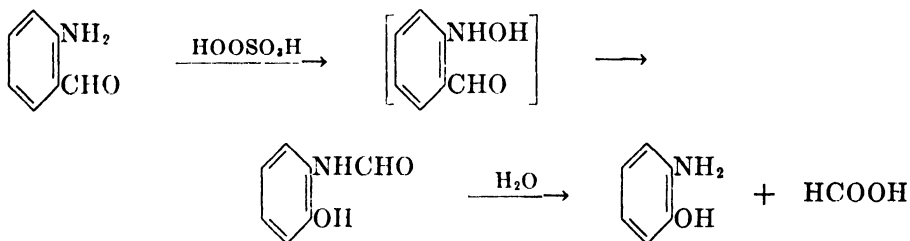
Wacek and Eppinger (68) proposed a similar mechanism for the Dakin reaction (alkaline hydrogen peroxide):

$$
\underset{\text{OH}}{\overset{\text{CHO}}{\bigcirc}} \longrightarrow \left[\underset{\text{OOH}}{\overset{\text{CHO}}{\bigcirc}}\right] \longrightarrow \underset{\text{OCHO}}{\overset{\text{OH}}{\bigcirc}} \longrightarrow \underset{\text{OH}}{\overset{\text{OH}}{\bigcirc}}
$$
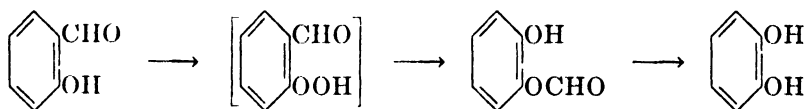
Their mechanism was supported by the fact that phenol is oxidized by hydrogen peroxide to hydroquinone and catechol.

But when Böeseken and his collaborators (8) showed that a free hydroxyl group was not necessary, it become obvious that a new mechanism was needed, at least for such cases. Wacek and Bézard (67) then developed reaction conditions which allowed the isolation of the intermediate catechol monoformate. They ran similar oxidations of methyl-substituted hydroxybenzaldehydes, hydrolyzing the reaction mixtures after treatment with diazomethane to methylate the unformylated hydroxyl. The product in each case was not just the substance predicted by their mechanism nor that predicted by the mechanism of page 405, but a mixture of both.

$$
\underset{\text{CH}_3}{\overset{\text{OH}}{\underset{}{\bigcirc}\text{CHO}}} \xrightarrow{\text{ROOH}} \xrightarrow{\text{CH}_2\text{N}_2} \xrightarrow{\text{H}_2\text{O}} \left\{ \begin{array}{l} \underset{\text{CH}_3}{\overset{\text{OH}}{\bigcirc}\text{OCH}_3} \\[2em] \underset{\text{CH}_3}{\overset{\text{OCH}_3}{\bigcirc}\text{OH}} \end{array} \right.
$$
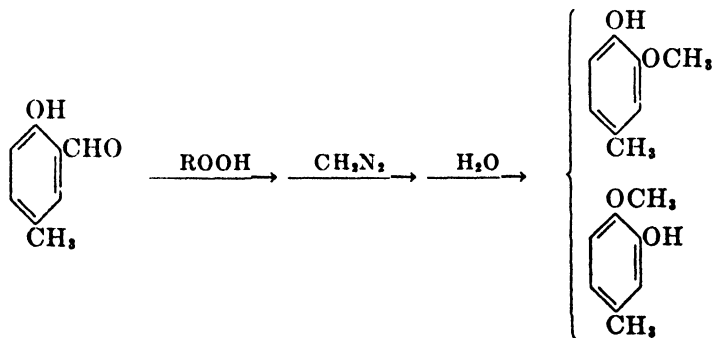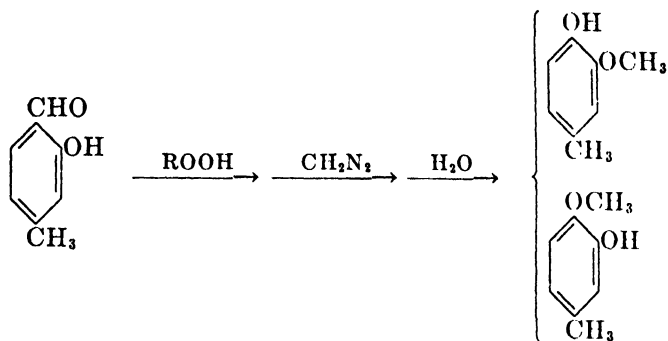
The mechanism which leads to the direct replacement of the formyl group by the formyloxy group is probably:
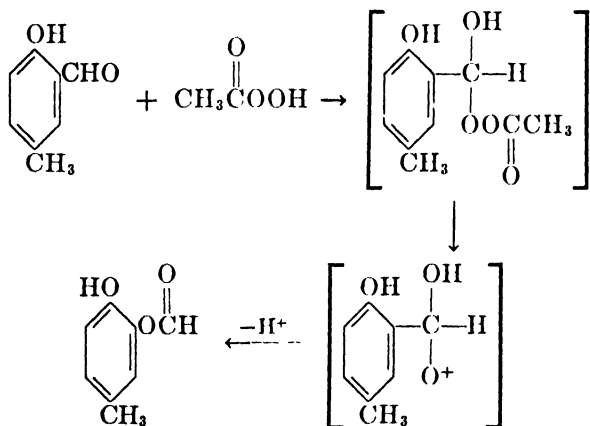
The other isomer is formed either by the mechanism of Wacek and Eppinger or by *trans*-esterification.

Aliphatic aldehydes are subject to the same sort of reaction. Acetaldehyde with hydrogen peroxide gives not only acetic acid but also some methane, probably from a methyl radical (6, 27). Propionaldehyde gives some acetic acid, formic acid, carbon dioxide, and ethane (6).

IV. OXIDATION OF ALCOHOLS

Decomposition of peroxides is not the only source of oxygen radicals and cations. Oxygen radicals are very probably produced, for example, in the photolysis of alkyl hypochlorites. Thus (11):

$$(CH_3)_3COCl \xrightarrow{h\nu} \left[CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot \right] \rightarrow CH_3COCH_3 + CH_3Cl$$
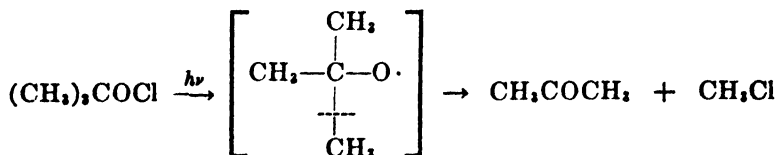
Mosher and his coworkers (47, 48) have found evidence of oxygen cations as intermediates in the chromic anhydride oxidation of alcohols:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad \xrightarrow[CH_3COOH]{CrO_3} \quad [RO^+] \quad \rightarrow$$

$$\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad + \quad \left[CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2^+ \right]$$

$$\downarrow$$

$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3 \quad \leftarrow \quad \left[CH_3-\underset{\underset{+}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3 \right]$$

(10 per cent yield)

$$CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CHOHCH_2CH_2CH_3 \quad \xrightarrow[CH_3COOH]{CrO_3} \quad CH_3CH_2CH_2CHO \quad +$$

$$\left[CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} \right] \quad \rightarrow \quad (CH_3)_3COH \qquad (47)$$

$$(C_6H_5)_3C-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-C_6H_5 \quad \xrightarrow[CH_3COOH]{CrO_3} \quad \begin{cases} (C_6H_5)_3COH \\ C_6H_5CHO \quad (22\ per\ cent) \\ C_6H_5COOH \end{cases} \qquad (48)$$

$$(C_6H_5)_3COH \quad \xrightarrow[CH_3COOH]{CrO_3} \quad (C_6H_5)_2CO \quad + \qquad \qquad (48)$$
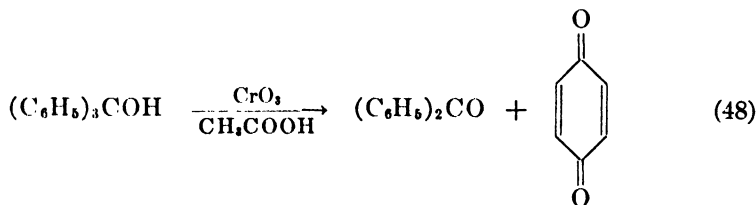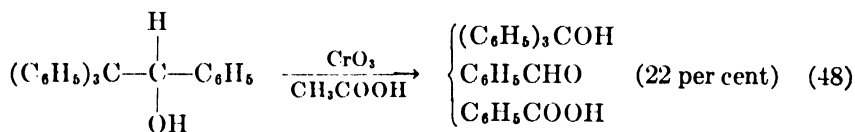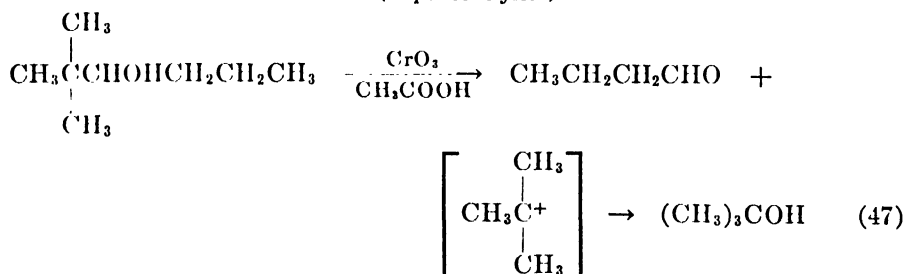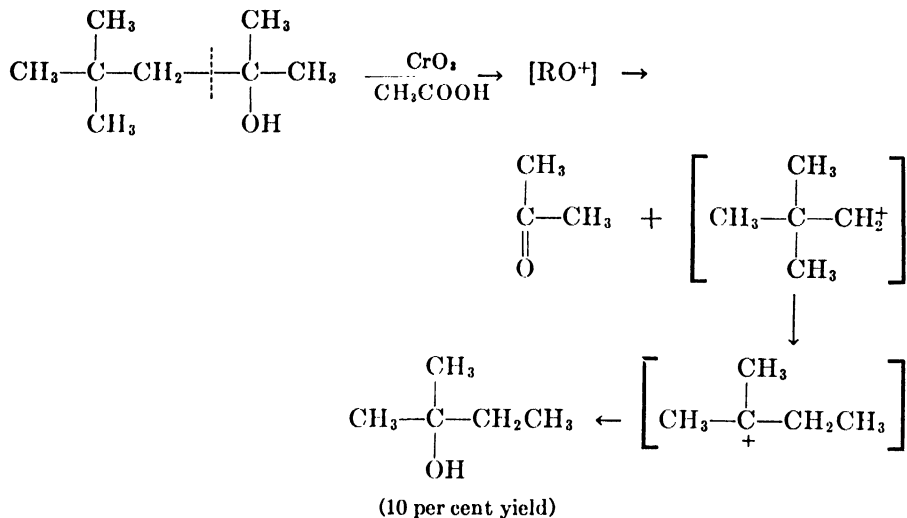
Fleury et al. (26) report the following reaction under conditions that leave acetone unscathed:

$$CH_3CHOHCH_2COOH \quad \xrightarrow[CrO_3]{HNO_3} \quad CH_3COOH \quad + \quad CO_2 \quad + \quad H_2O$$
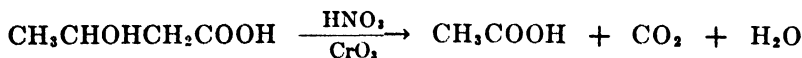
Since the reaction presumably does not involve acetoacetic acid and acetone, it is not unlikely that the first step is removal of a hydride ion from the alcohol, as in the reactions studied by Mosher.

There are a number of aromatic substitution reactions in which a carbinol group para to an amino group is replaced by a nitro group or bromine atom (14, 15, 24, 43). Such reactions go at very low temperatures. It is not at present possible to decide whether these reactions are true electrophilic substitutions, or examples of carbinol oxidation by the oxygen cation mechanism.

I wish to thank Professor Paul Doughty Bartlett for his many helpful suggestions.

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APPENDIX[2]

Since this review was written, but before it went to press, there have appeared several very important papers on oxygen cations; there is also considerable research in progress.

[2] Added August 29, 1949.

R. Criegee (Ann. **560,** 127 (1948)) has found that esters of decalin hydroperoxide decompose faster in media of higher dielectric constant. He therefore proposes that the reaction goes by way of an oxygen cation, which then rearranges with migration of a group from carbon to oxygen.

In the same paper Criegee proposes ionic mechanisms similar to those in this review for the ozonization of olefins and for the oxidation of ketones by Caro's acid. Waters (J. Chem. Soc. **1948,** 1574) has proposed ionic mechanisms for the oxidation of ketones with peracids in general. Strong confirmation for the Criegee–Waters mechanism is supplied by the kinetic study of S. L. Friess (J. Am. Chem. Soc. **71,** 2571 (1949)), who finds that the rate-determining step, in the case of perbenzoic acid, is the acid-catalyzed addition of the perbenzoic acid to the ketone. The rates of the oxidation reaction parallel the rates of semicarbazone formation for the same series of ketones.

H. H. Zeiss (J. Am. Chem. Soc. **70,** 858 (1948)) has proposed an oxygen cation intermediate for the chromic acid oxidation of tertiary alcohols. N. Kharasch, speaking at the Organic Symposium held at Madison, Wisconsin, in 1949, reported that cumene hydroperoxide decomposes either by an ionic mechanism to give acetone and phenol or by a radical mechanism to give acetophenone, depending on the reaction conditions. The present author (J. Am. Chem. Soc., to appear soon) has found that p-methoxy-p'-nitrobenzoyl peroxide may decompose by either the radical or the ionic mechanism. Ionic decomposition gives a p-methoxybenzoxy cation, which rearranges; the rearranged cation is isolated as the p-methoxyphenyl ester of p-nitrobenzoic carbonic anhydride.

THE MECHANISMS OF CHROMIC ACID OXIDATIONS

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CONTENTS

I. INTRODUCTION

Chromic acid has been long and successfully used as an oxidizing agent, for both preparative and analytical purposes. The procedures underlying the stoichiometric equations 1 and 2

$$HCrO_4^- + 3Fe^{++} + 7H^+ \rightarrow Cr^{+++} + 3Fe^{+++} + 4H_2O \tag{1}$$

$$2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 8H_2O \tag{2}$$
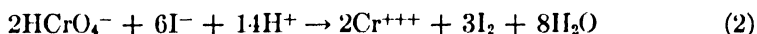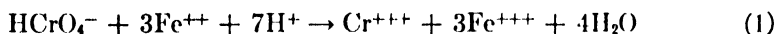
are among the classic methods of quantitative analysis. As a preparative reagent (65) chromic acid is customarily used, in aqueous sulfuric acid or in acetic acid solution, to oxidize primary alcohols or aldehydes to acids and to oxidize secondary alcohols to ketones. Chromic acid in acetic acid oxidizes toluene to benzoic acid, ethylbenzene to acetophenone, triphenylmethane to triphenylcarbinol, fluorene to fluorenone, and chrysene to chrysoquinone. Chromic anhydride, dissolved in acetic anhydride and sulfuric acid, oxidizes o-xylene to the tetraacetate of o-phthalaldehyde; Étard's reagent (chromyl chloride, CrO_2Cl_2) oxidizes substituted toluenes to the corresponding substituted benzaldehydes.

In all of the preparative reactions just cited, a carbon atom is the one oxidatively attacked; but chromates may also be used in many other reactions (e.g., the conversion of nitroso to nitro compounds or the conversion of sulfides to sulfones), where the oxidative attack is on an atom of an element other than carbon (nitrogen and sulfur, respectively, in the two examples cited). Evidently oxidation by chromates is one of the most versatile of chemical reactions.

It is not the purpose of this paper to attempt an exhaustive review of all the nstances where chromates have been used as oxidizing agents for either analytical or preparative purposes. Instead, attention will here be confined to those reactions which have been investigated with enough detail to throw some light on the mechanisms involved. Such reactions constitute but a small fraction of all those where hexavalent chromium has been used as an oxidizing agent; and even for those which have been more carefully investigated, the information at hand is still far from complete. Nevertheless, from the fragmentary data already available, it is clear that no single mechanism suffices to explain all the reactions of hexavalent chromium, and that intermediate products, in which chromium has the valence of four or five, occur in many (if not all) of the reactions in question.

In assigning a mechanism to the chromic acid oxidation of an organic compound, there are many questions to be answered. Is the reaction a transfer of an oxygen atom (or atoms) from the chromic acid to the organic molecule; is it primarily an electron transfer; or is it a dehydrogenation of the organic molecule? If it is a dehydrogenation, which hydrogen atom in the organic molecule is the one first attacked? What chromium-containing particles (ions or molecules) participate in the reaction? But underlying these and similar questions, there is another even more important one. The conversion of chromic acid to a compound of trivalent chromium is a three-electron change. The oxidation of organic compounds usually occurs in steps, but the final products almost always differ from the reactants by an even number of electrons. Just what is the nature of the electron transfer? Is the organic molecule oxidized in one-electron steps, so that free radicals are formed as intermediates, or is it oxidized directly in two-electron steps? (Three-electron transfers are, for various reasons, so improbable that they are here neglected.) Clearly, either of these alternatives for the first step in the reaction leads to an intermediate in which the chromium atom occurs in an unusual (and unstable) valence state for chromium. A one-electron transfer makes the hexavalent chromium atom temporarily pentavalent; a two-electron transfer makes it temporarily tetravalent.

The first problem here considered is that of the unusual and unstable valence states of chromium. It will be shown below that both pentavalent and tetravalent chromium are needed to account for the available data; divalent chromium may also participate in some of the reactions. The facts now known can be explained on the basis of the following assumptions:

(1) The standard oxidizing potential (in acid) of the (Cr^5–Cr^3) couple exceeds 1.75 volts; that of the (Cr^4–Cr^3) couple is probably even greater. (The standard oxidizing potential of the (Cr^4–Cr^3) couple is $+1.36$ volts.)

(*2*) Those reducing agents which preferentially lose one electron reduce chromic acid first to a molecule or ion containing pentavalent chromium; the subsequent steps of the reaction depend on the other properties of the reducing agent.

(*3*) Those reducing agents which preferentially lose two electrons reduce chromic acid in the following steps:

$$Cr^6 + H_2A \rightarrow Cr^4 + A \tag{3}$$

$$Cr^6 + Cr^4 \rightarrow 2Cr^5 \tag{4}$$

$$Cr^5 + H_2A \rightarrow Cr^3 + A \tag{5}$$
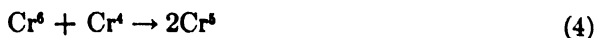
Here H_2A and A are the reduced and oxidized forms of the reducing agent; the first is converted to the second by a two-electron change.[2] Equation 4 is only stoichiometrically significant; it is probably the sum of two or more steps.

(*4*) When chromic acid acts upon a mixture of two reducing agents, A and B, of which A preferentially loses one electron, whereas B preferentially loses two, the reaction is a combination of the two schemes just described.

The (partial) reaction mechanisms based on these principles (1 to 4) require two special explanations. It is necessary first to show that some materials are actually oxidized in two-electron steps; and second, to discuss the phenomenon called induced oxidation.

For many years it has been customary to classify reducing agents as (*1*) those which can donate one and only one electron, and (*2*) those which generally if not always donate two electrons. This classification appears justified, despite the efforts of a few chemists to show that all oxidations proceed exclusively by one-electron steps. In this field, the most interesting single experiment is that of Shaffer (61; *cf.* 56), who showed that reaction 6, between ceric ion and thallous ion, although thermodynamically possible, is very slow.

$$2Ce^{++++} + Tl^+ \rightarrow 2Ce^{+++} + Tl^{+++} \tag{6}$$

Shaffer suggested that a triple collision (suggested by the stoichiometry of equation 6) is unlikely, and that, in the absence of such a triple collision, the reaction can not occur without the formation of an unstable and unknown compound of divalent thallium as an intermediate in the reaction. Furthermore he showed that, in conformity with his theory, the reaction between thallous and ceric ions is catalyzed by salts of manganese. Presumably the manganese atom, which can undergo either one- or two-electron changes, functions as a go-between in the transfer of electrons from the thallous to the ceric ion.

It must be admitted, however, that this theory, although reasonable, is not necessarily correct, since the electrostatic repulsion between ceric and thallous

[2] Designations such as Cr^6 or Cr^5 are used where the nature of the particular ion or molecule containing a chromium atom of the indicated valence cannot be identified (or is immaterial); symbols such as H_2CrO_4, Cr^{+++}, etc., refer to particular molecular or ionic species. Since the formulas for ions containing Cr^5 etc., are unknown, equations in which they appear are balanced only for gross valence change.

ions might in itself be sufficient to prevent reaction. (The slow ferrous–ferric (68) exchange is presumably an example of this sort.)

Browne (40; see 17) made a similar classification of oxidizing agents. He found that, when hydrazine is oxidized, two different sets of products are obtained depending on the oxidizing agent used. According to this scheme, these oxidizing agents fall into two classes: those which easily take up only one electron at a time, and those which easily take up two electrons at a time. These two classes are known respectively as the monodeëlectronators and the dideëlectronators. The statement that an oxidizing agent "easily" takes up one (or two) electrons merely means that such a reaction leads to compounds in which the reduced atom occurs only in known and relatively stable valence states. It is highly improbable that all oxidation–reduction reactions can be explained without taking dideëlectronators into consideration.

II. INDUCED OXIDATIONS

The best evidence for the existence (as unstable intermediates) of pentavalent and tetravalent chromium compounds is the phenomenon known as induced oxidation. A favorite and early example of this phenomenon, discovered by Schönbein (60) in 1858, is the oxidation of iodide to iodine by dichromate, an oxidation which may be induced by ferrous iron. In dilute acid (0.001 N) and at low concentrations reaction 2 between chromate and iodide ions is very slow; so also is reaction 7 between ferric and iodide ions. Under these conditions, however, reaction 1 between ferrous and dichromate ions is rapid.

$$2HCrO_4^- + 6I^- + 14H^+ \rightarrow 2Cr^{+++} + 3I_2 + 8H_2O \tag{2}$$

$$2Fe^{+++} + 2I^- \rightarrow 2Fe^{++} + I_2 \tag{7}$$

$$HCrO_4^- + 3Fe^{++} + 7H^+ \xrightarrow{\text{rapid}} Cr^{+++} + 3Fe^{+++} + 4H_2O \tag{1}$$
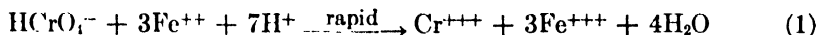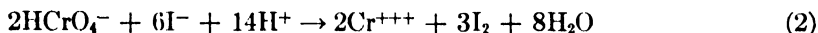
When a solution containing dilute mineral acid, chromic acid, and iodide is treated with a solution of a ferrous salt, iodine is rapidly liberated; usually the stoichiometry is represented by an equation such as equation 8.

$$HCrO_4^- + Fe^{++} + 2I^- + 7H^+ \xrightarrow{\text{rapid}} Cr^{+++} + Fe^{+++} + I_2 + 4H_2O \tag{8}$$
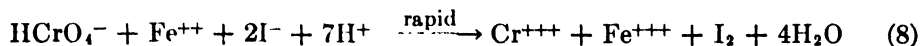
It appears that, in the presence of a ferrous salt, iodide ion is rapidly oxidized under experimental conditions where, in the absence of the ferrous salt, that ion is relatively inert. Here the ferrous ion is said to "induce" the oxidation of the iodide.

Another important early example of induced oxidation (also studied by Schönbein (60)) is that (55) of indigo by dichromate; here the inducing agent is oxalic acid. This oxidation was utilized in the industry of the day to produce white designs on blue fabrics. The cloth, dyed with indigo, was printed with a dichromate salt. When the cloth thus printed was treated with oxalic acid, the indigo was bleached only where it was in contact with dichromate. Schönbein showed that sulfuric acid could not be used to replace oxalic; the reaction was

therefore a genuine case of induced oxidation. The term "induced oxidation" was introduced by Kessler (39). In an excellent paper published in 1863 he tabulated the then known reactions of this type. Among his examples was the arsenite-induced oxidation of manganous ion by chromic acid, a reaction which he himself had discovered (38) two years previously. He also listed several alleged examples (37; see also 24) of induced oxidation which had been observed before his paper was published; these reactions, however, have never been investigated well enough to be historically important.

Induced oxidations fall into two classes, which may be illustrated by the induced oxidation of iodide and of manganous ions. The induced oxidation of iodide yields two equivalents of iodine for each equivalent of the inductor oxidized. On the other hand, the induced oxidation of manganous salts to manganic salts or to manganese dioxide yields one equivalent of oxidized manganese for each two equivalents of inductor oxidized. In any induced oxidation the "induction factor" is defined as the ratio of the number of equivalents of the reducing agent oxidized to the number of equivalents of the inductor oxidized. In the reactions cited above, the induction factor for the iodide oxidation is 2 and that for the manganous ion oxidations is 0.5.

In all induced chromic acid oxidations (with one possible exception cited below) where the induction factor has been determined, it has been found to be either 2 or 0.5. That is to say, of the three oxidation equivalents supplied by each mole of $HCrO_4{}^-$, either one or two are used for the induced oxidation; this precise stoichiometry suggests Cr^4 or Cr^5 as the valence state of the chromium atom in the compound which participates as an intermediate in the reaction. How these stoichiometrical considerations indicate the valence of the unstable intermediate may be shown by considering the chromic acid oxidation of iodide ions which is induced by ferrous ions, and the chromic acid oxidation of manganous ions which is induced by arsenite.

The oxidation of iodide by chromic acid may be induced by ferrous ions under conditions where iodide is not oxidized either by chromic acid or by ferric ion alone, hence in such a reaction mixture there must be formed an oxidizing agent more powerful or more rapid (or both) than dichromate. Since the ratio of the number of equivalents of iodide oxidized to the number of equivalents of inductor (ferrous ion) oxidized is 2:1, this more powerful intermediate oxidizer which reacts with the iodide ions probably contains pentavalent chromium. The scheme given in equations 9, 10, and 11 (where hypoiodite is assumed as an intermediate) is one of several which are stoichiometrically correct; it anticipates the results of the kinetic investigations presented later on (see footnote 2).

$$Cr^6 + Fe^{++} \leftrightarrows Cr^5 + Fe^{+++} \tag{9}$$

$$Cr^5 + I^- \rightarrow Cr^3 + IO^- \tag{10}$$

$$2H^+ + I^- + IO^- \rightarrow I_2 + H_2O \tag{11}$$
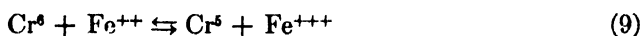
The oxidation of manganous salts by chromic acid is induced by arsenite under conditions where manganous salts are not oxidized by chromic acid alone. Hence

in such a reaction mixture there must be formed some oxidizing agent more powerful or more rapid (or both) than dichromate. Since the ratio of the number of equivalents of manganous salt oxidized to the number of equivalents of inductor (arsenite) oxidized is 1:2, this more powerful intermediate oxidizer which reacts with manganous salt probably contains tetravalent chromium. The scheme given in equations 12, 13, and 14 is a possible one for the reaction in question.

$$Cr^6 + As^3 \rightarrow Cr^4 + As^5 \tag{12}$$

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \tag{13}$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \tag{14}$$

Summing up these arguments, an induction factor of 2 indicates that the active oxidizing agent is pentavalent chromium, whereas an induction factor of 0.5 indicates that this agent is tetravalent chromium. Since both induction factors have been observed, chromium probably exists in both of these intermediate valence states.

Induced oxidation is in some respects similar to catalysis; but whereas in catalysis the catalyst is recovered unchanged, in induced oxidation the "inductor" is consumed. Moreover, the amount of inductor so consumed usually bears a stoichiometric relation to the amount of product formed. For reaction 2, catalysis by ferrous ion is thermodynamically possible; but the corresponding reaction

$$3Mn^{++} + 2HCrO_4^- + 2H^+ \rightarrow 3MnO_2 + 2Cr^{+++} + 2H_2O \tag{15a}$$

at pH > 0 is thermodynamically impossible (46). Indeed, in the absence of arsenite, reaction 15a proceeds slowly from right to left. Nevertheless, the reaction

$$6H^+ + 2HCrO_4^- + 2H_3AsO_3 + Mn^{++} \rightarrow$$

$$2Cr^{+++} + 2H_3AsO_4 + MnO_2 + 4H_2O \tag{15b}$$
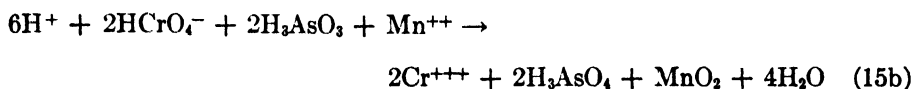
is thermodynamically possible, since the standard free-energy change for this induced reaction is negative, owing to the fact that the inductor is consumed in the process.

The above discussion of the stoichiometry of induced oxidations is actually a considerably simplified version of the facts. Clearly, when arsenite is oxidized in the absence of manganous ion, the chromium in either of the intermediate valence states (Cr^4 or Cr^5) is consumed in the oxidation of more arsenite. (The mechanism for this follow-up reaction corresponds to that given in equations 4 and 5; it will be discussed later.) Therefore, when manganous ion and arsenite are both present, they compete for the tetravalent chromium; the higher the concentration of the manganous ion, the more successful will this reagent be in the competition. Since similar considerations apply to all induced oxidations, any stoichiometry corresponding to an induction factor of 2, or of 0.5, is to be regarded as a theoretical limit, which is approached only at high concentrations

of the substance the oxidation of which is induced. Every induced oxidation so far investigated has yielded data which support this conclusion.

An asymptotic approach to the induction factor of 2 is shown in table 1A, where the reaction is the chromic acid oxidation of iodide induced by vanadous sulfate; an asymptotic approach to the induction factor of 0.5 is shown in table

TABLE 1A

Asymptotic approach to an induction factor of 2

Oxidation of varying amounts of iodide by 0.009 M K₂Cr₂O₇; reaction induced by 0.00044 M VSO₄ in the presence of 0.007 M H₂SO₄ (data of Luther and Rutter)*

RATIO OF MOLES OF I⁻ TO MOLES OF V⁺⁺	OBSERVED INDUCTION FACTOR
4.5	1.22
8.7	1.43
19.8	1.47
39.3	1.51
91.2	1.61
192.4	1.68
459.	1.87
903.	1.96
1530.	1.99

* In the last two experiments, the concentration of V⁺⁺ is below that given at the top of the table.

TABLE 1B

Asymptotic approach to an induction factor of 0.5

Oxidation of 0.04 M manganous ion by 0.005 M K₂Cr₂O₇; reaction induced by varying amounts of H₃AsO₃ in the presence of 3.5 M H₂SO₄ (concentrations approximate) (data of Lang and Zwerina)

RATIO OF MOLES OF Mn⁺⁺ TO MOLES OF As₂O₃	OBSERVED INDUCTION FACTOR
3.2	0.15
3.6	0.30
4.1	0.41
5.6	0.45
7.2	0.46
10.	0.46
14.	0.50
28.	0.51

1B, where the reaction is the chromic acid oxidation of manganous ion induced by arsenious acid.

The induced oxidations involving chromic acid are of two types: (a) those where the chromic acid acts as an oxidizing agent and (b) those where it acts as an inductor. In reactions of type (a) (some of which are listed in table 2) one reducing agent (the inductor, IR) induces the rapid chromic acid oxidation of the acceptor, H₂A, under conditions where, in the absence of IR, H₂A is either not attacked or only very slowly attacked by chromic acid. In reactions of type

(b) (some of which are listed in table 3) chromic acid, IOx, induces the rapid oxidation of a reducing agent, H_2A, by some oxidizing agent, Ox, under conditions where, in the absence of chromic acid, H_2A is either not attacked or only very slowly attacked by Ox.

TABLE 2

Induced oxidations in which Cr^6 is the oxidizing agent

INDUCTOR (IR)	OXIDIZING AGENT (Ox)	SUBSTANCE OXIDIZED (ACCEPTOR) (H_2A)	INDUCTION FACTOR	REFERENCE
Fe^{++}	CrO_3	I^-	2	Manchot and Wilhelms[a] Benson[b]
H_2AsO_3	CrO_3	I^-	2	De Lury[c]
$VOSO_4$	CrO_3	I^-	2	⎱
$(VO)_2SO_4$	CrO_3	I^-	2	⎰ Luther and Rutter[e]
VSO_4	CrO_3	I^-	2	
Ti^{+++}	CrO_3	I^-	2	Manchot and Richter[f]
$UOSO_4$	CrO_3	I^-	0.5–0.7	Luther and Rutter[e]; Manchot[g]
H_2AsO_3	CrO_3	Mn^{++}	0.5	Lang and Zwerina[d]
$CH_3CHOHCH_3$	CrO_3	Mn^{++}	0.5	Watanabe and Westheimer[h]
Fe^{++}	CrO_3	Br^-	Unknown	⎱
$VOSO_4$	CrO_3	Br^-		⎰ Luther and Rutter[e]
Ti^{+++}	CrO_3	Br^-		
H_2TeO_3	CrO_3	Ferrion		⎱ Lang[i]
Ferrion	CrO_3	H_2TeO_3	Unknown	⎰
$K_4Fe(CN)_6$	CrO_3	Tartaric acid		
SO_2	CrO_3	Tartaric acid		
Sb_2O_3	CrO_3	Tartaric acid	Unknown	⎬ Kessler[j]
SnO	CrO_3	Tartaric acid		
As_2O_3	CrO_3	Tartaric acid		
Oxalic acid	CrO_3	Indigo	Unknown	Schönbein[k]

[a] MANCHOT, W., AND WILHELMS, O.: Ann. **325**, 105, 125 (1902).
[b] BENSON, C.: J. Phys. Chem. **7**, 1 (1903).
[c] DE LURY, R. E.: J. Phys. Chem. **11**, 239 (1907).
[d] LANG, R., AND ZWERINA, J.: Z. anorg. Chem. **170**, 389 (1928).
[e] LUTHER, R., AND RUTTER, T. F.: Z. anorg. Chem. **54**, 1 (1907).
[f] MANCHOT, W., AND RICHTER, P.: Ber. **39**, 488 (1906).
[g] MANCHOT, W.: Ber. **39**, 1352, 3510 (1906).
[h] WATANABE, W., AND WESTHEIMER, F. H.: J. Chem. Phys. **17**, 61 (1949).
[i] LANG, R.: Mikrochim. Acta **3**, 113 (1938).
[j] KESSLER, F.: Pogg. Ann. **119**, 218 (1863).
[k] SCHÖNBEIN, C. F.: J. prakt. Chem. **75**, 108 (1858).

To explain the induced oxidations of the type listed in table 3, it is probably necessary to assume the presence of bromites, or of compounds in which iron has a valence higher than three, etc. The reactions where chromic acid induces the oxidation of arsenite or stannous chloride by atmospheric oxygen will be discussed later.

III. KINETICS OF CHROMIC ACID OXIDATIONS

A. *The oxidation of isopropyl alcohol*

The chromic acid oxidation of isopropyl alcohol (79) has been studied with care and in detail. The reaction proceeds smoothly to completion as shown in equation 16. An essentially quantitative yield of acetone is obtained.

$$3CH_3CHOHCH_3 + 2HCrO_4^- + 8H^+ \rightarrow 3CH_3COCH_3 + 2Cr^{+++} + 8H_2O \quad (16)$$
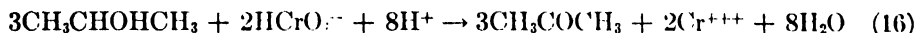
Here kinetic studies have been used to identify the particular compound of hexavalent chromium which, under given conditions, serves as the oxidizing agent. Since this part of the investigation is independent of the rest of the study, it can be treated separately.

An aqueous solution of chromic acid certainly contains the following ions: CrO_4^{--}, $HCrO_4^-$, and $Cr_2O_7^{--}$. In addition, it may possibly contain other species

TABLE 3

Induced oxidations in which Cr⁶ is the inductor

INDUCTOR (IOx)	OXIDIZING AGENT (Ox)	SUBSTANCE OXIDIZED (ACCEPTOR) (H₂A)	REFERENCE
Cr^6	O_2	H_2AsO_3	Luther and Rutter[a]
Cr^6	$HBrO_3$	H_2AsO_3	Luther and Rutter
Cr^5	$FeCl_3$	H_2AsO_3	Luther and Rutter
Cr^6	$HClO_3$	H_2AsO_3	Luther and Rutter
Cr^6	$H_2S_2O_8$	H_2AsO_3	Luther and Rutter
Cr^6	O_2	$SnCl_2$	Luther and Rutter

[a] LUTHER, R., AND RUTTER, T. F.: Z. anorg. Chem. **54**, 1 (1907).

such as $HCr_2O_7^-$, $H_2Cr_2O_7$, or H_2CrO_4. The ionization constant, K_{17}, for the $HCrO_4^-$ ion (*cf.* equation 17) is about 10^{-7}; hence, in dilute aqueous acid, the concentration of CrO_4^{--} ions is negligible. The ionization constant, K_{18}, for the $HCr_2O_7^-$ ion is not known, but careful work (42) has shown that this constant is large, hence, in solutions where pH $\geqslant$ 1 the ionization (*cf.* equation 18) may be

$$HCrO_4^- \rightleftarrows H^+ + CrO_4^{--} \quad (17)$$

$$HCr_2O_7^- \rightleftarrows H^+ + Cr_2O_7^{--} \quad (18)$$
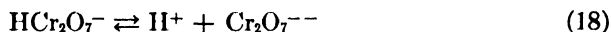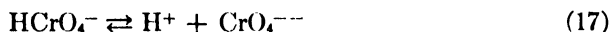
considered essentially complete. Consequently, of all the ions involving hexavalent chromium, the only ones present in large concentrations in solutions of dilute mineral acid are $HCrO_4^-$ and $Cr_2O_7^{--}$. These ions are in equilibrium with each other, according to the equation:

$$H_2O + Cr_2O_7^{--} \rightleftarrows 2HCrO_4^- \quad (19)$$
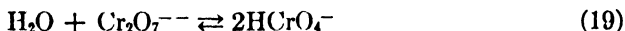
Reaction 19, unlike reactions 17 and 18, has an equilibrium the position of which is independent of pH. This position varies with the total concentration of hexavalent chromium (hereafter referred to as the gross concentration of chromic acid). There have been several attempts (36, 59, 62, 80) to measure the equilib-

rium constant, K_{19}. Methods based on the spectrophotometric analysis of chromic acid solutions have so far failed (30), because the absorption spectra of these solutions deviate only slightly from Beer's law. Hence it must be concluded that the acid chromate ion ($HCrO_4^-$) and the dichromate ion ($Cr_2O_7^{--}$) have approximately the same absorption spectra. Methods based on the freezing points of potassium dichromate solutions have been more successful. The observed freezing-point depressions are considerably greater than those which would be expected if the only ions present were K^+ and $Cr_2O_7^{--}$. Since the second ionization constant of chromic acid, K_{17}, is very small (about 10^{-7}), the additional ions necessary to account for the observed depressions cannot be H^+ ions; hence they must be $HCrO_4^-$ ions. The only precise freezing-point data are those of Sherrill (62), which were obtained before the idea of activity coefficients had been introduced. These data have, however, recently been recomputed (22, 73) by a method which involves activity coefficients based on the interionic attraction theory. The results confirm those obtained by Neuss and Rieman, whose work is next described.

The best quantitative determination of the equilibrium constant, K_{19}, is that of Neuss and Rieman (54), who used a glass electrode to study the acidity of solutions of potassium dichromate. They evaluated their data in terms of the two equilibrium constants, K_{17} and K_{19}. Since this evaluation was complicated by ionic strength effects, extrapolation to infinite dilution proved very difficult. Nevertheless the treatment was successful, and the two equilibrium constants (K_{17} and K_{19}) were evaluated. The constant (K_{17}) thus obtained proved to be of the same order of magnitude as that obtained by other investigators. The equilibrium constant for the acid chromate–dichromate equilibrium at infinite dilution, is 0.023.

$$\frac{(HCrO_4^-)^2}{(Cr_2O_7^{--})} = 0.023 \text{ mole/liter} \qquad (20)$$

In the investigation of the chromic acid oxidation of isopropyl alcohol it was possible to determine which of the two chromium-containing species (cf. equation 19) is the active oxidizing agent (79). As a rough approximation, the rate of this oxidation is proportional to the first powers of the concentrations of the alcohol and of the gross chromic acid; it is proportional to the second power of the concentration of the hydrogen ions. More precisely, the rate of oxidation depends in a complex way upon the gross chromic acid concentration. But when the initial gross concentration of chromic acid is varied stepwise over an eighty-fold range, a definite pattern becomes clear. In the very dilute solutions (0.0005–0.005 M) the rate is proportional to the gross chromic acid concentrations; in more concentrated solutions, the rate is less than that to be expected from the results obtained with dilute solutions. Furthermore, individual experiments with concentrated solutions no longer lead to good rate constants. But when the same data are recomputed on the assumption that the only active oxidizing species is the acid chromate ion, $HCrO_4^-$, the data all lead to the same satisfactory rate constant. In order to make this latter computation, the equilibrium constant,

K_{20}, of Neuss and Rieman was used in a slightly modified form which takes account of the ionic strengths of the solutions employed. The conclusion (i.e., that the active oxidizing agent is the acid chromate ion, $HCrO_4^-$) does not depend upon the exact value of the equilibrium constant, K_{20}, but only upon its approximate magnitude. The experiments in question are illustrated by figures 1 and 2. It will later be shown that other chromic acid oxidations besides that of isopropyl alcohol can be simplified and explained in terms of the equilibrium of equation 19.

The more precise kinetic picture thus obtained of the chromic acid oxidation of isopropyl alcohol indicates that the reaction rate is proportional to the first power of the acid chromate ion concentration, the first power of the isopropyl alcohol concentration, and the second power of the hydrogen-ion concentration. The rate-determining step therefore involves one acid chromate ion, one alcohol molecule, and two hydrogen ions. Since the chromium atom must change valence by three units, and the alcohol molecule must change by only two, some ion or molecule containing chromium in an intermediate valence state (Cr^4 or Cr^5) must take part in the reaction.

A further fact which supports the conclusion just reached is that isopropyl alcohol, like arsenious acid, induces the chromic acid oxidation of manganous ion to manganese dioxide. A quantitative study (72) of this induced oxidation has shown that one equivalent of manganese dioxide is produced for every two equivalents of isopropyl alcohol oxidized. That is to say, the induction factor is 0.5. This result indicates that the substance which oxidizes manganous ion is very probably tetravalent, not pentavalent, chromium, but it does not indicate whether the tetravalent chromium is produced directly from hexavalent chromium or indirectly from pentavalent chromium. The reaction kinetics, however, settle this point. The rate at which chromic acid is consumed in the oxidation of isopropyl alcohol is decreased by manganous ion to an extent which depends on the concentration of manganous ion present. The effect of even 10^{-5} moles per liter of manganous ion can easily be detected; when the concentration of manganous ion is greater than 0.001 mole per liter, the rate approaches asymptotically a value approximately one-half of that found in the absence of this ion.

A satisfactory mechanism for the chromic acid oxidation of isopropyl alcohol must account quantitatively for the diminution in reaction rate produced by manganous ion. One mechanism which fulfills this condition is:

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3 \tag{21}$$

$$Cr^4 + CH_3CHOHCH_3 \rightarrow Cr^2 + CH_3COCH_3 \tag{22}$$

$$Cr^2 + Cr^6 \rightarrow Cr^3 + Cr^5 \tag{23}$$

$$Cr^5 + CH_3CHOHCH_3 \rightarrow Cr^3 + CH_3COCH_3 \tag{24}$$

and

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \tag{13}$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \tag{14}$$
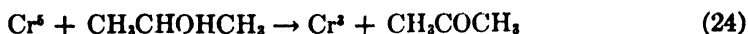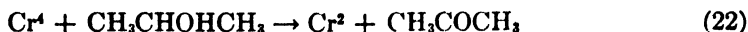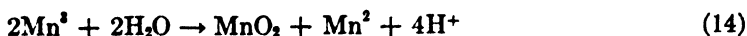
In most of these reactions, the hydrogen ion is omitted for the sake of convenience. It will later be shown that the mechanism given in equations 21 to 24 is one of four possibilities.
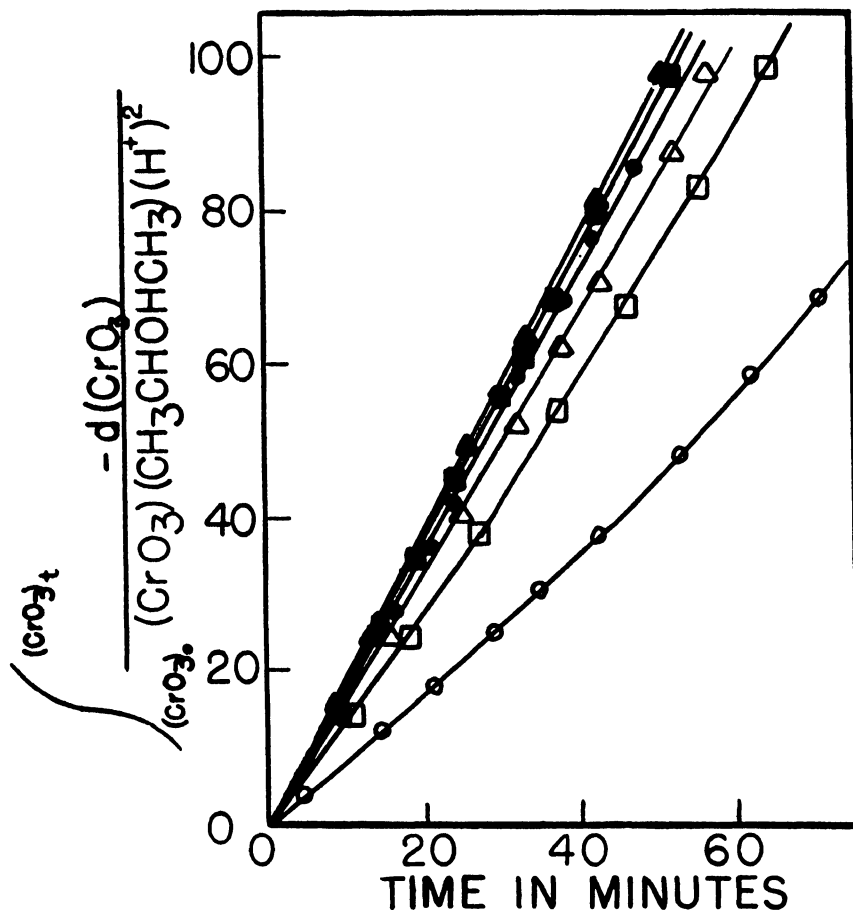
FIG. 1. Graphical representation of the equation

$$\int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(CrO_3)(CH_3CHOHCH_3)(H^+)^2} = kt$$

which assumes that all ions or molecules containing hexavalent chromium are oxidizing agents for isopropyl alcohol. Concentrations of H^+ and $CH_3CHOHCH_3$ were 0.2694 M and 0.2001 M, respectively. The various chromic acid concentrations are represented by the following symbols:

O = 0.04316 M	△ = 0.004316 M	■ = 0.001079 M
□ = 0.01079 M	● = 0.002158 M	▲ = 0.0005316 M

The scheme just given accounts for all the facts now known. First, since it involves the oxidation of manganous ions by tetravalent chromium, it accounts

for the induction factor of 0.5. Second, it accounts for the fact that manganous ion cuts in half the total rate at which hexavalent chromium is consumed. For hexavalent chromium is consumed not only in reaction 21 but also in reaction 23. If tetravalent chromium is reduced by manganous ion (reaction 13) before
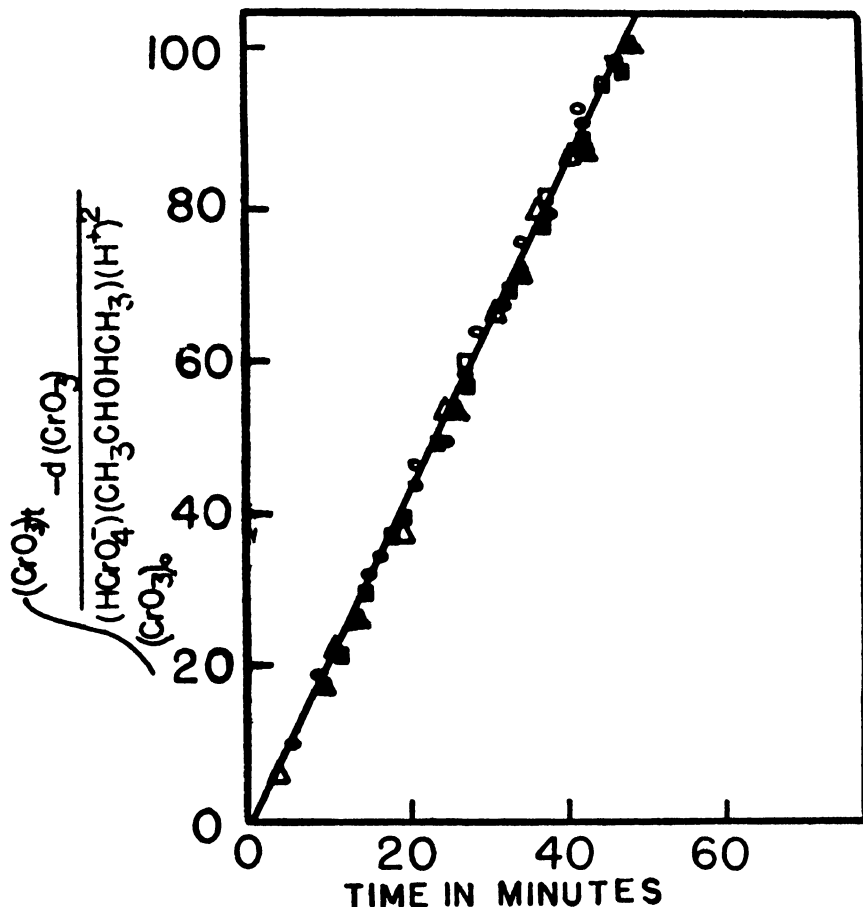
FIG. 2. Graphic representation of the equation

$$\int_{(CrO_3)_0}^{(CrO_3)_t} \frac{-d(CrO_3)}{(HCrO_4^-)(CH_3CHOHCH_3)(H^+)^2} = kt$$

which assumes that only $HCrO_4^-$ ions oxidize isopropyl alcohol. The data are the same as those shown in figure 1.

it has a chance to undergo reactions 22 and 23, the rate of consumption of Cr^6 is necessarily cut exactly in half.

As already stated, the scheme just advanced is consistent with all the known facts. To show that no other scheme will fit these facts is, as in all such cases, impossible. But in the present instance it may be shown that, within certain

limits, four mechanisms are the only ones possible. The limits here chosen are logically arbitrary but chemically reasonable. The most important conditions are (a) only the chemical species $HCrO_4^-$, Cr^5, Cr^4, Cr^3, Cr^2, H_2A, $HA\cdot$, A, and $HO\cdot$ need be considered and (b) when relatively stable and relatively unstable particles occur together in a reaction mixture, the unstable particles (especially when they belong to a species present only at high dilution) do not react with one another to the practical exclusion of reactions between unstable and stable particles. When such is the fact, reactions between unstable particles may be neglected. A full discussion of this point and the other necessary limitations is included in the paper by Watanabe and Westheimer (72).

The kinetic data can be explained by reaction schemes other than the ones here advanced if the limitations described above are discarded (16). However, until and unless, at some future time, evidence is discovered inconsistent with the mechanism here advanced, this mechanism appears relatively probable; if such conflicting evidence is eventually discovered, it will probably be apparent which of the assumptions (a), (b), etc., here made is at fault. According to the limitation just set forth, reactions such as

$$Cr^5 + HA\cdot \rightarrow Cr^4 + A \tag{25}$$

or

$$2Cr^5 \rightarrow Cr^6 + Cr^4 \tag{26}$$
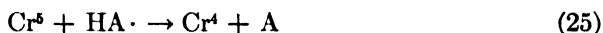
may be neglected.

Thus the only reactions which need be considered are:

$$Cr^6 \;\; + H_2A \rightarrow Cr^4 \;\; + A \tag{27a or 21}$$

$$Cr^6 \;\; + H_2A \rightarrow Cr^5 \;\; + HA\cdot \tag{27b}$$

$$Cr^5 \;\; + H_2A \rightarrow Cr^3 \;\; + A \tag{27c}$$

$$Cr^5 \;\; + H_2A \rightarrow Cr^4 \;\; + HA\cdot \tag{27d}$$

$$Cr^4 \;\; + H_2A \rightarrow Cr^2 \;\; + A \tag{27e}$$

$$Cr^4 \;\; + H_2A \rightarrow Cr^3 \;\; + HA\cdot \tag{27f}$$

$$Cr^6 \;\; + HA\cdot \rightarrow Cr^5 \;\; + A \tag{27g}$$

$$Cr^6 \;\; + Cr^4 \;\; \rightarrow 2Cr^5 \tag{27h}$$

$$Cr^6 \;\; + Cr^2 \;\; \rightarrow Cr^5 \;\; + Cr^3 \tag{27i}$$

$$Cr^6 \;\; + Cr^2 \;\; \rightarrow 2Cr^4 \tag{27j}$$

$$Cr^4 \;\; + H_2O \rightarrow Cr^3 \;\; + HO\cdot \tag{27k}$$

$$HO\cdot + H_2A \rightarrow H_2O + HA\cdot \tag{27l}$$

This list includes all the possible reactions where isopropyl alcohol is oxidized in a one-electron step to form a free radical or in a two-electron step to form acetone.

In the presence of manganous ion, the reactions of the following set (set 28) must also be taken into account:

$$Mn^2 + Cr^5 \rightarrow Mn^3 \ + Cr^4 \qquad (28a)$$

$$Mn^2 + Cr^5 \rightarrow MnO_2 + Cr^3 \qquad (28b)$$

$$Mn^2 + Cr^4 \rightarrow Mn^3 + Cr^3 \qquad (28c \text{ or } 13)$$

$$Mn^2 + Cr^4 \rightarrow MnO_2 + Cr^2 \qquad (28d)$$

$$2Mn^3 + 2H_2O \rightarrow MnO_2 + Mn^2 + 4H^+ \qquad (28e \text{ or } 14)$$
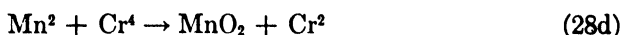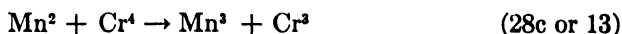
In terms of the reactions of sets 27 and 28, there is only one mechanism (reactions 27a, 28c, 28e; earlier presented as reactions 21, 13, 14) which is consistent with observed effects of manganous ions; there are exactly four mechanisms (those represented by the set of reactions 27a, 27e, 27i, 27c, by the set 27a, 27h, 27c, by the set 27a, 27f, 27g, 27c, and by the set 27a, 27k, 27l, 27g, 27c) which are consistent with the facts observed in the absence of manganous ions. Each of these four mechanisms, however, starts with the reaction:

$$HCrO_4^- + CH_3CHOHCH_3 \rightarrow Cr^4 + CH_3COCH_3 \qquad (21 \text{ or } 27a)$$

It is therefore highly probable that this two-electron change is the first step in the oxidation of isopropyl alcohol by chromic acid.

So far, it has been established that the reaction between acid chromate ion and isopropyl alcohol is a two-electron change. It will next be shown that, during the rate-controlling step of this reaction, the secondary hydrogen atom is the one removed. This conclusion follows from the following experiments.

The rate of oxidation of 2-deutero-2-propanol (1) has been measured (78) under experimental conditions identical with those used for the oxidation of ordinary isopropyl alcohol. The deuterium compound reacts only about one-sixth as fast as does the hydrogen compound. This fact is considered to prove that the secondary hydrogen atom is removed in the rate-controlling step of the oxidation. For if the attack were elsewhere (e.g., upon the hydroxylic hydrogen atom), replacement of the secondary hydrogen atom by deuterium could scarcely cause so large a change in rate. If and only if the secondary hydrogen is directly involved in the rate-controlling step does so large a change of rate become reasonable.

Decreases in rate similar to the one here adduced have been noted in other instances (50, 57, 81) where the transfer of a hydrogen (or deuterium) atom is involved in the rate-controlling step of a reaction. Furthermore, the experimental facts are reinforced by a simple theory. The zero-point energy of a bond is equal to $h\nu_0/2$, where ν_0 is the fundamental vibration frequency of the bond in question. Both theoretically and experimentally, it is found that a hydrogen atom vibrates faster with respect to the molecule than does a heavier deuterium atom. The zero-point energy of a carbon–hydrogen bond is therefore considerably greater than that of a carbon–deuterium bond. If, during a reaction, the carbon–hydrogen (or carbon–deuterium) bond is broken, the vibration in question can no longer

occur; there is then no longer any difference in zero-point energy between the system which originally had the C—H bond and that which originally had the C—D bond. (Actually, this statement is an oversimplification of the facts; the idea here presented is only approximately correct.) A little consideration shows that in the case under discussion, the activation energy for the reaction of the deuterium compound should exceed that for the reaction of the hydrogen compound by (approximately) the difference in zero-point energies between the C—H and the C—D bonds. It follows, therefore, that the deuterium compound should react more slowly than does the hydrogen compound.

The facts so far established do not completely determine the mechanism of the chromic acid oxidation of isopropyl alcohol; consistent with these facts are the two reaction schemes 29 and 30a, 30b.

$$
\begin{bmatrix} H \\ O \\ HOCrO \\ O \\ H \end{bmatrix}^+ + \underset{\overset{|}{CH_2}}{\overset{CH_3}{\overset{|}{HCOH}}} \rightarrow \underset{\overset{|}{H}}{\overset{H}{\overset{|}{HOCrOH}}} + \underset{\overset{|}{CH_3}}{\overset{CH_3}{\overset{|}{C}}}=OH^+ \qquad (29)
$$

$$HCrO_4^- + 2H^+ + CH_3CHOHCH_3 \underset{\longleftarrow}{\overset{fast}{\longrightarrow}}$$

$$[(CH_3)_2CHOCrO_3H_2]^+ + H_2O \quad (30a)$$

$$[(CH_3)_2CHOCrO_3H_2]^+ + H_2O \overset{slow}{\longrightarrow} (CH_3)_2CO + H_2CrO_3 + H_3O^+ \quad (30b)$$
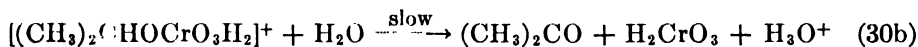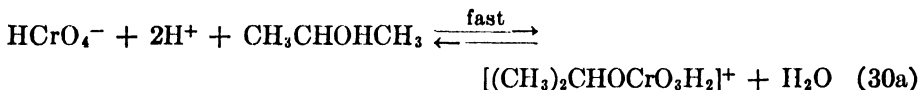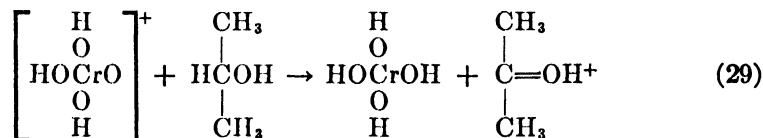
Consistent with the esterification mechanism (equations 30a, 30b) is the fact that unstable chromic acid esters of several tertiary alcohols have been prepared (34, 53, 76); consistent with the direct removal of a hydride ion by chromic acid (equation 29) is the fact that diisopropyl ether can be oxidized to acetone by chromic acid in sulfuric acid solution (13), and that this oxidation is not preceded by a hydrolysis of the ether to isopropyl alcohol. Further study is needed to decide between the two mechanisms cited (cf., however, the work of Mosher discussed below).

The mechanism of the chromic acid oxidation of isopropyl alcohol in aqueous solution has so far been partly elucidated. It should not, however, be inferred that this mechanism applies to the chromic acid oxidation of any other compound in aqueous solution, or to the chromic acid oxidation of any substance in any non-aqueous solvent (e.g., acetic acid). More such oxidation reactions must be investigated before generalization will be safe.

Here it is well to consider certain evidence obtained from other oxidations which may perhaps bear upon the mechanism of the isopropyl alcohol oxidation already discussed. Waters (58, 74, 75) has shown that oxygen is absorbed during the chromic acid oxidation in acetic acid solution of many alcohols, ethers, etc. Reference has already been made (see table 3) to the absorption of oxygen during chromic acid oxidations. Waters interpreted his observations to mean that chromic acid oxidation must necessarily involve organic free radicals as unstable intermediates. But since oxygen absorption is characteristic of chromic acid

oxidations, both inorganic and organic, it is more probable that some compound containing pentavalent, tetravalent, or divalent chromium is the species which absorbs oxygen. Nevertheless, the possibility of free-radical intermediates remains open; they have been ruled out only in the first step of the oxidation of isopropyl alcohol in dilute chromic acid.

Mosher (51, 52) has advanced the hypothesis that chromic acid oxidation of certain alcohols proceeds by way of a transitory intermediate formed by removing a hydride ion from the hydroxyl group of the alcohol. His theory implies that the rate-controlling step is the formation of this intermediate, which subsequently reacts by either one or both of two indicated paths. Clearly, no such intermediate can occur in the oxidation of isopropyl alcohol under the conditions already discussed; the experiments with the deuterated alcohol rule out this possibility. Mosher advanced his hypothesis to explain his discovery that methyl-t-amyl-carbinol when oxidized by chromic acid yields 10 per cent of t-amyl alcohol; this and similar facts can be explained equally well by mechanisms other than the one he gives (e.g., a decomposition of a chromic acid ester along somewhat different lines than those indicated by equation 30b). An alternative mechanism (by way of carbonium ions) for the chromic acid oxidation of certain tertiary alcohols has recently been suggested by Zeiss (83).

B. The oxidation of arsenious acid

In 1904, the oxidation of arsenious acid by chromic acid was studied by De Lury (18, 19) under the direction of Professor Lash Miller. De Lury acidified his solutions with sulfuric acid; unfortunately he happened to work in a region (0.01–0.05 M acid) where the second ionization of this acid is incomplete. His data have therefore been recomputed (table 4) using 0.02 mole per liter for the ionization constant for the HSO_4^- ion at 0°C. (31, 43). The data thus recomputed show that the reaction rate is roughly proportional to the square of the concentration of hydrogen ion. Investigations over a broader range of acidity are required to determine whether the discrepancies shown by these and similar data are significant or whether they fall within the experimental error.

De Lury also found, at least as a first approximation, that the rate in the oxidation of arsenious acid is proportional to the 0.7 power of the concentration of the chromic acid. However, when his data are recomputed, taking into account the equilibrium (equation 20) between dichromate and acid chromate ion, it appears that this rate (as in the oxidation of isopropyl alcohol) is nearly proportional to the concentration of acid chromate ion (see table 5). Thus clearly the true rate equation for the chromic acid oxidation of arsenious acid is

$$-d(CrO_3)/dt = k(H_3AsO_3)(HCrO_4^-)(H^+)^2 \qquad (31)$$

This equation is strictly analogous to the one for the oxidation of isopropyl alcohol.

Several interesting oxidations are induced by the chromic acid–arsenious acid reaction; among them are those of iodide, bromide, and manganous ions. The last of these will be considered first.

Lang (44, 45) showed that arsenite induces the chromic acid oxidation of manganous ion to manganese dioxide and manganic ion. (In dilute aqueous acid, these species are in equilibrium with manganous ion.) Since, under the given experimental conditions, the oxidation of manganous ion to manganic ion (or MnO_2) is thermodynamically impossible, it follows that the observed oxidation

TABLE 4

Recomputation of De Lury's data (influence of H^+ concentration)

EXPERIMENT NO.	CONCENTRATION OF CHROMIC ACID AS $Cr_2O_7^{--}$	CONCENTRATION OF H^+ (RECOMPUTED)	k(De Lury)/$(H^+)^2$
	moles per liter	*moles per liter*	*(moles per liter)$^{-2}$ min.$^{-1}$*
5............	0.00298	0.164	214
1 and 4........	0.00298	0.055	238

TABLE 5

Recomputation of De Lury's data (influence of chromic acid concentration)

EXPT. NO.	$K_2Cr_2O_7$	As_2O_3	H_2SO_4	k(De Lury) or $\frac{1}{2.3}k_1$	$(HCrO_4^-)$	(H^+)	$\frac{10^{-5} k_1}{(HCrO_4^-)(H^+)^2}$
	moles per liter $\times 10^3$	*moles per liter $\times 10^3$*	*moles per liter $\times 10^2$*	*min.$^{-1}$*	*moles per liter $\times 10^3$*	*moles per liter $\times 10^2$*	*min.$^{-1}$ (moles per liter)$^{-3}$*
1......	2.98	0.0497	9.68	0.058	4.19	15.2	1.38
2.... ...	5.96	0.0497	9.68	0.110	7.00	15.2	1.57
3........	11.94	0.0497	9.68	0.178	11.25	15.2	1.57
4........	2.98	0.0298	9.68	0.052	4.19	15.2	1.24
5........	2.98	0.0497	19.36	0.164	4.19	27.6	1.18
6........	2.98	0.0497	15.50	0.107	4.19	22.7	1.14
7........	0.67	0.0833	8.07	0.115	1.19	13.1	1.30
8........	0.67	0.0833	8.07	0.114	1.19	13.1	1.29
9........	0.67	0.1667	8.07	0.116	1.19	13.1	1.31
10........	0.67	0.0833	16.14	0.318	1.19	23.7	1.10
11........	0.67	0.0417	8.07	0.114	1.19	13.1	1.29
12........	0.67	0.0417	16.14	0.300	1.19	23.7	1.03
13........	1.33	0.0833	8.07	0.217	2.17	13.1	1.34
14........	1.33	0.0417	8.07	0.200	2.17	13.1	1.23
15........	0.67	0.0417	4.03	0.044	1.19	7.05	1.71
Average..							1.31 ± 0.13

of manganous ion must involve an intermediate containing tetravalent or pentavalent chromium. For this particular reaction, Lang showed that the induction factor is 0.5, i.e., two electrons are contributed by the arsenite for each electron contributed by the manganous ion. More precisely, the induction factor approaches 0.5 as a limit (see table 1) when the manganous-ion concentration is high. This fact indicates that the intermediate contains tetravalent chromium.

On the other hand, when an arsenite in dilute aqueous acid is oxidized by chromic acid in the presence of iodide the induction factor is 2, i.e., two equivalents of iodide are oxidized for each one of arsenite. This fact indicates that iodide is here oxidized by pentavalent chromium. Thus, in the oxidation of arsenite by chromic acid either tetravalent or pentavalent chromium may, under suitable conditions, occur as an intermediate. With regard to the reaction induced by iodide, it is of interest that the overall rate of reduction of chromic acid is unaffected by the iodide. This fact was discovered by De Lury. He found that, with increasing iodide concentration, the induction factor approached 2. In any par-
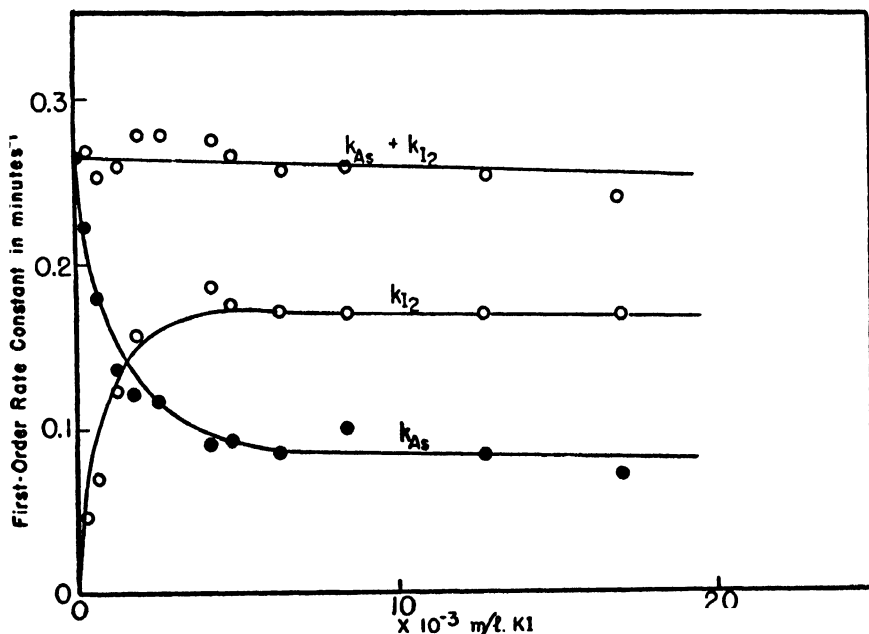
FIG. 3. The arsenate-induced oxidation of iodide by dichromate. Rate constant for the formation of iodine is k_{I_2}, that for the formation of arsenate is k_{As}.

ticular experiment, however, the sum of the rates of production of iodine and arsenate was just equal to the rate at which chromate was reduced in a reaction mixture containing no iodide. His data are illustrated in figure 3.

The most satisfactory reaction scheme so far proposed to account for the above facts is the following:

$$HCrO_4^- + As^3 \rightarrow Cr^4 + AsO_4^- \qquad (32a; cf. 12)$$

$$Cr^4 + Cr^6 \rightarrow 2Cr^5 \qquad (32b \text{ or } 4)$$

$$Cr^5 + As^3 \rightarrow Cr^3 + AsO_4^- \qquad (32c)$$
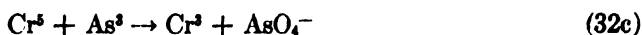
This scheme calls for the formation of both tetravalent and pentavalent chro-

mium as intermediates. Either of these can then function as an oxidizing agent in an induced oxidation, as shown in the following equations:

$$Cr^4 + Mn^2 \rightarrow Cr^3 + Mn^3 \tag{15}$$

$$Cr^5 + 2I^- \rightarrow Cr^3 + I_2 \tag{33}$$

Furthermore, according to the given scheme the overall rate of reduction of hexavalent chromium should be (as it is) unaffected by the addition of iodide. As previously noted (see equation 4) equations 32b and 32c are only stoichiometrically correct; they may represent the sum of other more complex reactions.

Most of the schemes which might be proposed as alternatives to scheme 32 involve the assumption that some compound containing tetravalent arsenic occurs as a transitory intermediate in the reaction. Such an assumption cannot now be shown to be erroneous. But it seems unwise to postulate a reaction in which two very unstable compounds (one of pentavalent chromium and one of tetravalent arsenic) are simultaneously produced.

$$HCrO_4^- + As^3 \rightarrow Cr^5 + As^4 \tag{34}$$

However, if this unlikely postulate is accepted, it is still difficult to plan a proper sequence of subsequent reactions which involve tetravalent chromium and at the same time account for the kinetics of the overall reaction. Most of those schemes which involve tetravalent arsenic, tetravalent chromium, and pentavalent chromium lead to the conclusion that the reaction should be autocatalytic —a conclusion incompatible with experiment. In the absence of any evidence to the contrary, mechanism 32 appears adequate for the chromic acid oxidations of arsenious acid.

C. The oxidation of ferrous ion

The kinetics of the oxidation of ferrous ion by chromic acid was developed in 1903. In two excellent papers, Clara Benson (4), who also worked under the direction of Professor Lash Miller, determined the rate of the reaction, varying the initial concentration of each of the reactants (ferrous ion, ferric ion, chromic acid, and hydrogen ion) independently, and by a factor not less than 2. Her work strongly suggests the following rate equation:

$$-\frac{d(Cr^6)}{dt} = k \frac{(Cr^6)^{1.7}(Fe^{++})^2(H^+)^2}{(Fe^{+++})} \tag{35}$$

The unusual fractional exponent of the chromic acid concentration which appears in this equation will be discussed later. Attention is here directed to the fact that the rate is proportional directly to the square of the ferrous-ion concentration[3] and inversely to the first power of the ferric-ion concentration. The

[3] The dependence of the rate on the square of the ferrous-ion concentration was established by experiments in which the initial concentration of ferrous ion was varied. Regret-

inverse dependence of the reaction rate on ferric-ion concentration is further supported by Gortner (28). He found that fluoride (which forms a strong complex with ferric but not with ferrous ion (26)) greatly accelerates the oxidation, probably by reducing the concentration of ferric ion. But all of this work does not fully establish the quantitative dependence of the rate on the inverse first power of the ferric-ion concentration. Here (for want of evidence to the contrary) this dependence will be assumed.

Wagner (70) interprets the observed decrease in reaction rate with increase in concentration of ferric ion as follows. The first step in the reaction is a reversible one in which ferric ion is produced.

$$Cr^6 + Fe^{++} \rightleftarrows Cr^5 + Fe^{+++} \tag{9}$$
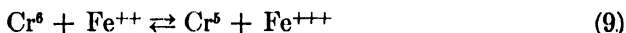
Subsequently pentavalent chromium reacts, in a rate-controlling step, with ferrous ion. Such a pair of reactions leads to the observed dependence of the reaction rate upon the concentrations of ferrous and ferric ions. Wagner has suggested two alternative schemes for the second (rate-controlling) step.

$$Cr^5 + Fe^{++} \rightarrow Cr^4 + Fe^{+++} \text{ (rate controlling)} \tag{36}$$

$$Cr^4 + Fe^{++} \rightarrow Cr^3 + Fe^{+++} \tag{37}$$

or

$$Cr^5 + Fe^{++} \rightarrow Cr^3 + Fe^4 \text{ (rate controlling)} \tag{38}$$

$$Fe^4 + Fe^{++} \rightarrow 2Fe^{+++} \tag{39}$$
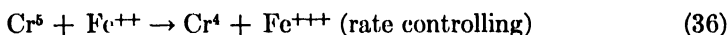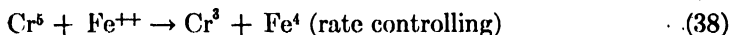
In 1903 Benson (4) studied quantitatively the ferrous ion-induced oxidation of iodides by chromic acid. The induction factor is 2, i.e., two iodide ions are oxidized for each ferrous ion. This fact strongly suggests that the iodide ions are oxidized by some compound of pentavalent chromium. Probably the reaction is

$$Cr^5 + I^- \rightarrow Cr^3 + IO^- \tag{10}$$

$$2H^+ + IO^- + I^- \rightarrow I_2 + H_2O \tag{11}$$

tably there is a typographical error (revealed by recomputation of the original data) in Miss Benson's record of her experiment No. 1. The appropriate constants are

EXPERIMENT	k, COMPUTED FOR A REACTION OF ORDER n IN FERROUS ION		
	$n = 1$	$n = 2$	$n = 3$
No. 1.....................	0.21	0.66	2 (approx.)
No. 2.....................	0.12	0.71	4 (approx.)

The ferrous-ion concentration was twice as high in experiment No. 2 as in No. 1; only for the second order of this concentration is k approximately constant.

At high concentrations of iodide, the equation for the rate of formation of iodine is

$$d(I_2)/dt = k\ (H^+)_4(CrO_3)^{1.5} \frac{(I^-)(Fe^{++})}{(Fe^{+++})} \qquad (40)$$

This equation indicates that iodide competes successfully with ferrous ion for the pentavalent chromium. Furthermore, at high concentrations of iodide, chromic acid disappears several times as fast as it does in the absence of iodide. This fact supports the hypothesis that iodide reacts with pentavalent chromium. If reaction 10 (instead of 36 or 38) is the rate-controlling step, then the overall rate of formation of iodine must depend on the concentrations of I^- and Fe^{++} in the way shown by the experimentally determined kinetic equation (equation 40).

The asserted dependence of the rate on the fourth power (see equation 40) of the hydrogen-ion concentration should be reinvestigated; the later and more precise work of Wagner (*vide infra*) suggests that the third power is more probable.

Wagner and Preiss (70) have carefully studied the competition between ferrous ion and iodide for pentavalent chromium. In successive experiments they varied the concentrations of ferrous ion, chromate, iodide, and acid over wide ranges. Assuming the mechanism already proposed (*cf.* equations 9–11 and 36–39), the amount of iodine formed depends primarily upon the relative concentrations of the iodide and ferrous ions.

$$Cr^6 + Fe^{++} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cr^5 + Fe^{+++} \qquad (9)$$

$$Cr^5 + Fe^{++} \overset{k_3}{\longrightarrow} products \qquad (36\ or\ 38)$$

$$Cr^5 + I^- \overset{k_4}{\longrightarrow} Cr^3 + IO^- \qquad (10)$$
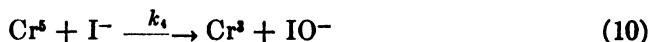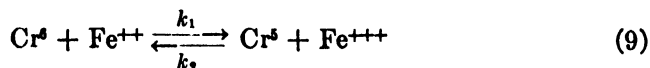
If v_1 is the rate of reactions 36 or 38, and v_2 is that of reaction 10, then

$$\frac{v_1}{v_2} = \frac{k_3(Fe^{++})}{k_4(I^-)} \quad \text{and} \quad \frac{k_3}{k_4} = \frac{(I^-)}{(Fe^{++})} \frac{v_1}{v_2} \qquad (41)$$

The ratio v_1/v_2 is the ratio of the rate of formation of ferric ion (after allowing for reaction 9) to the rate of formation of iodine; near the beginning of the reaction the ratio of these rates is measured by the ratio of the yields. Wagner and Preiss found that, at constant acidity, the ratio k_3/k_4 (based upon yield determinations in accordance with equation 41) is in fact constant. This result agrees with the interpretation of the reaction given above. They also found that, with varying acidity, $k_3(H^+)/k_4$ rather than k_3/k_4 is constant; this fact means that the rate-controlling step of the reaction of pentavalent chromium with iodide involves one more hydrogen ion than does the reaction of pentavalent chromium with ferrous ion. Since the overall rate of the chromate–ferrous ion

reaction depends (*cf.* equation 35) on the square of the hydrogen-ion concentration, the induced oxidation of iodide should depend upon the third power (rather than the fourth power; *cf.* equation 40) of the hydrogen-ion concentration.

Although the mechanism of the oxidation of iodide by chromate, as induced by ferrous ion, is thus satisfactorily explained, there remain two alternative paths for the oxidation of ferrous ion by pentavalent chromium. One of these involves tetravalent chromium, the other tetravalent iron. (There are other oxidations (11, 27, 33) which can be explained by assuming the formation of unstable intermediate compounds of tetravalent iron.) The data so far available do not fully justify a choice between the two.

According to equations 35 and 40, in the chromic acid oxidation of ferrous ion the observed reaction rate is approximately proportional to the 1.5–1.7 power of the chromic acid present. This fractional power in the kinetic equation remains to be explained. When the acid chromate ion is the sole oxidizing agent (e.g., in the oxidation of arsenite; see equation 31), the oxidation rate is apparently proportional to a fractional power (between 0.5 and 1.0) of the total chromic acid. The exponent greater than unity (that is, 1.5–1.7) for the chromic acid concentration in the rate equation 35 or 40 suggests that here the active oxidizing agent is the dichromate ion, $Cr_2O_7^{--}$. The concentration of this ion must vary (*cf.* equation 20) as the square of the gross concentration of chromic acid, wherever that concentration is small. The observations of Benson, although not in good quantitative agreement with the hypothesis that $Cr_2O_7^{--}$ is the active oxidizing agent, certainly suggest that such is the fact.

Since, however, the hexavalent chromium and ferrous ion are assumed to be in equilibrium (see equation 9) with pentavalent chromium and ferric ion, this explanation is valid only if the pentavalent chromium is here present as a complex with hexavalent chromium. (For example, if equation 9 may be rewritten

$$Cr_2O_7^{--} + Fe^{++} \rightleftarrows Cr_2O_7^{---} + Fe^{+++} \tag{42}$$
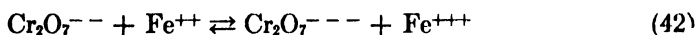
the ion $Cr_2O_7^{--}$ is given merely as a hypothetical example of a Cr^5–Cr^6 complex.)

Such an assumption of a new chromium-containing species, however, would require reconsideration of the reaction schemes for the chromic acid oxidation of isopropyl alcohol (72).

D. *The oxidation of formic acid*

Quantitative investigations of chromic acid oxidations, with the exception of the studies already discussed, have not been highly successful. Nevertheless, some of them deserve further mention, and among such is the oxidation of formic acid. The rate of this reaction has not yet been investigated over a wide range of initial concentrations of chromic acid; consequently the appropriate kinetic equation is still unknown. The reaction rate, like that of the oxidation of isopropyl alcohol, is diminished by manganous ion, but where the concentration of Mn^{++} is moderate, this rate approaches one-third (rather than one-half) of the rate when no Mn^{++} is present (21). These facts suggest (but do not prove) that

the mechanism for the oxidation of formic acid is similar to that for the oxidation of isopropyl alcohol. The difference in the factor by which Mn^{++} diminishes the rate is easily explained. In the oxidation of formic acid, the conditions are such that no MnO_2 accumulates in the solution. Wagner therefore suggested that manganous ion catalyzes the disproportionation of tetravalent or pentavalent chromium to chromic ion and to chromate. Of the several sets of reactions which would account for the experimental facts, reaction 43 is a sequence which may occur in the absence of manganous ion and reaction 44 is a sequence which may occur in the presence of that ion. (These sequences, although tentative, are here preferred to the ones suggested by Wagner.)

$$HCrO_4^- + HCOOH \rightarrow CO_2 + Cr^4 \tag{43a}$$

$$Cr^4 + Cr^6 \rightarrow 2Cr^5 \tag{43b or 4}$$

$$Cr^5 + HCOOH \rightarrow Cr^3 + CO_2 \tag{43c}$$

and

$$HCrO_4^- + HCOOH \rightarrow CO_2 + Cr^4 \tag{44a}$$

$$3Cr^4 \text{ (in steps, catalyzed by } Mn^{++}) \rightarrow 2Cr^3 + HCrO_4^- \tag{44b}$$
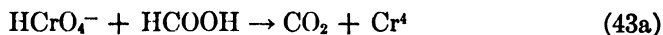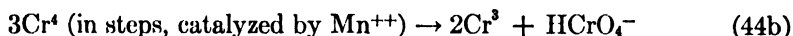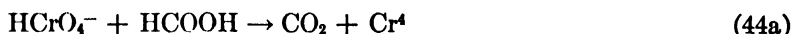
The sets of equations 43 and 44 account for the observed fact that in the presence of manganous ion the rate of disappearance of chromic acid is only one-third as great as it is in the absence of that ion.

The rate of oxidation of formic acid by chromic acid is also diminished by addition of cerous salts. A complete kinetic study of the oxidation under these conditions has not yet been carried out, but since the only known valence states of cerium are three and four, the valence of the cerium must increase by one during the reaction. Hence, the cerous salt probably reacts with a compound containing tetravalent chromium. This conclusion is consistent with the general mechanism (equations 43 and 44) already proposed for the reaction.

Snethlage (64) investigated the chromic acid oxidation of formic acid in solutions containing 1–60 per cent sulfuric acid. The function pH as applied to such solutions has little or no meaning; the only acidity function useful under the stated conditions is Hammett's H_0 function (29). This function, applied to dilute aqueous solutions, approaches pH asymptotically; applied to concentrated sulfuric acid, it is a logarithmic function of the tendency of the solvent to transfer a proton to an uncharged base. Any reaction which proceeds by way of an activated complex made up of various (electrically neutral) molecules and one proton obeys the relation:

$$\log k + H_0 = \text{constant} \tag{45}$$

This relation agrees approximately with Snethlage's finding that the oxidation rate in 60 per cent sulfuric acid is 30,000 times as fast as the rate in 5 per cent sulfuric acid. This agreement supports the hypothesis that one proton reacts with a formic acid molecule and the appropriate chromate ion. It is reasonable

to assume that the mechanism for the chromic acid oxidation of formic acid is similar to that for the oxidation of isopropyl alcohol.

E. The oxidation of phosphorous acid

The oxidation of phosphorous acid by chromic acid has been investigated by Dhar (21). Manganous ion diminishes the oxidation rate by two-thirds, a fact which suggests a reaction scheme analogous to that proposed for formic acid (equations 43 and 44).

F. The oxidation of aldehydes

The rates of the chromic acid oxidations of some aromatic aldehydes (48) in acetic acid–sulfuric acid solutions have been studied in some detail. From the data available, it is impossible to determine which particular ion of hexavalent chromium is the active oxidizing agent. On the other hand, the effect which the structure of the aldehyde exercises on the oxidation rate has been thoroughly tested. The nitrobenzaldehydes are oxidized considerably more rapidly than is benzaldehyde, which in turn is oxidized more rapidly than is p-methoxybenzaldehyde. The interpretation of these facts is by no means unambiguous; further investigations are needed to permit valid conclusions concerning the mechanisms of the various reactions.

G. The oxidation of inorganic iodides

Studies of the chromic acid oxidation of iodide ion, although they have been extensive, have not led to any fully satisfactory reaction mechanism. In dilute solutions of chromic acid the oxidation rate is proportional to a power of the chromic acid concentration (18) slightly less than 1; very probably the true oxidizing agent (as in the oxidations of isopropyl alcohol and arsenite) is the acid chromate ion. The reaction rate depends in a complex way on the concentrations of the iodide and hydrogen ions (2); apparently there is in the rate equation a term in $(H^+)(I^-)$ and one in $(H^+)^2(I^-)^2$. But at present little more can be said about this highly important reaction.

H. The oxidation of uranyl ion

The chromic acid oxidation of uranyl ion (49) has not been investigated in detail. However, in this reaction, the induction factor for iodide is not 2 but approximately 1; and this fact sets the reaction in question apart from all other induced oxidations of iodide. Without further experimentation, no mechanism can here be definitely established. Nevertheless, the fact that compounds of pentavalent uranium are known suggests the following scheme as a working hypothesis.

$$UO^{++} + Cr^6 \rightarrow UO_2^{++} + Cr^4 \tag{46a}$$

$$UO^{++} + Cr^4 \rightarrow U^5 + Cr^3 \tag{46b}$$

$$U^5 + Cr^6 \rightarrow U^6 + Cr^5 \tag{46c}$$

$$UO^{++} + Cr^5 \rightarrow UO_2^{++} + Cr^3 \tag{46d}$$

or

$$Cr^5 + 2I^- \rightarrow Cr^3 + I_2 \qquad \text{(46e or 33)}$$
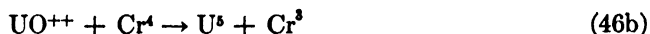
Competition between a set of reactions such as 46 (which implies an induction factor of 0.5) and the normal type of induced oxidation of iodide (which implies an induction factor of 2) would account for the intermediate values (0.7–1.0) experimentally obtained for the induction factor in the oxidation of uranyl ion.

I. The oxidation of oxalic, lactic, and malic acids

Studies of the chromic acid oxidation of oxalic, lactic, and malic acids have shown that the kinetics of these reactions are extremely complex. First and foremost, there are wide differences in reaction products. Oxalic acid, as expected, is oxidized to carbon dioxide, but lactic acid is oxidized not at the hydroxyl but at the carboxyl group (14):

$$8H^+ + 2HCrO_4^- + 3CH_3CHOHCOOH \rightarrow$$
$$3CH_3CHO + 3CO_2 + 2Cr^{+++} + 8H_2O \quad (47)$$
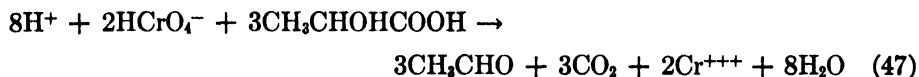
Reaction 47 probably does not involve an oxidation of lactic acid to pyruvic acid, followed by a decarboxylation; for pyruvic acid, under the experimental conditions in question, undergoes further oxidation (15) much more rapidly than it undergoes decarboxylation (3). Presumably the lactic acid is attacked at the carboxyl group. Although the nature of the products obtained by chromic acid oxidation from other hydroxy acids has not been fully determined, reactions analogous to 47 are probably not infrequent.

The rate of the chromic acid oxidation of oxalic acid does not depend in any simple manner upon the concentrations of the reactants (20, 35), nor does it increase monotonically with increase in the concentration of added sulfuric acid (63). The rate constant for the oxidation in sulfuric acid solution is much greater than that for the thermal decomposition in the same solution (12, 47).

$$HOOCCOOH \rightarrow CO_2 + CO + H_2O \qquad (48)$$
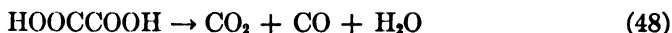
Hence, the oxidation must clearly involve a direct attack of the oxidizing agent upon the organic acid (or ion). Furthermore, the rates of oxidation of both oxalic and lactic acids are considerably increased by the addition of small amounts of manganous ion (20, 21). Further information about these oxidations has been obtained from photochemical studies.

J. Photochemical oxidations

Although most chromic acid oxidations have been studied only in the dark, experiment has shown that some of them are accelerated by light. Bhattacharya and Dhar (6) showed that, in the chromic acid oxidation of citric, tartaric, and lactic acids, the quantum yields range from 100 to 1000. The reactions are thus clearly photochemical chain reactions of some sort. By contrast, Bowen (7, 8, 9, 10) and his coworkers showed that when the lower aliphatic alcohols are photo-

chemically oxidized by dichromates,[4] the quantum yield never exceeds 2. There is of course no assurance that the mechanism of any particular photochemical oxidation by chromic acid bears any resemblance to the mechanism of the corresponding dark reaction. However, the results of the two photochemical investigations just quoted are consistent with the mechanisms hereafter proposed for the dark reactions.

The oxidation of isopropyl alcohol by chromic acid is kinetically simple. It is characterized by the following facts: (*1*) The only organic product is acetone. (*2*) The reaction rate depends upon small integer powers of the concentrations of the reactants (isopropyl alcohol, hydrogen ion, and $HCrO_4^-$ ion). (*3*) Manganous ion decreases the reaction rate; the reaction induces the oxidation of Mn^{++} to MnO_2. (*4*) The corresponding photochemical oxidation has a low integer quantum yield. On the other hand, the oxidation of lactic acid, for example, is very complex: (*1*) The point of oxidative attack is at the carboxyl, not at the hydroxyl group. (*2*) The reaction rate does not depend upon small integer powers of the concentrations of the reactants. (*3*) The reaction is catalyzed, not retarded, by the addition of manganous ion. (*4*) The corresponding photochemical oxidation is characterized by a long reaction chain. Evidently the mechanism for the oxidation of lactic acid (and of oxalic and malic acids) must be quite different from that for the oxidation of isopropyl alcohol. A detailed study of the oxidations of the acids mentioned may well reveal that these reactions involve organic free radicals as intermediates.

IV. COMPOUNDS OF PENTAVALENT AND TETRAVALENT CHROMIUM

In the preceding discussions of the mechanisms of chromic acid oxidations, the existence of unstable intermediates containing pentavalent and tetravalent chromium has been inferred from kinetic data. Hence, it is appropriate to examine the evidence for the existence of stable compounds containing chromium in these unusual valence states.

There are several known compounds which probably contain pentavalent chromium. The most important series (77) of such compounds was discovered by Wienland; it consists of the potassium, rubidium, cesium, ammonium, pyridinium, and quinolinium salts of the anion $CrOCl_4^-$. These salts are prepared by treating acetic acid solutions of chromium trioxide with dry hydrogen chloride, and then adding to the mixture a solution of the appropriate metal (or substituted ammonium) chloride. The formulas of the substances thus prepared suggest that they contain pentavalent chromium. Their oxidizing power corresponds to that anticipated for compounds containing chromium with this valence; and in non-ionizing solvents the molecular weight of the pyridinium compound corre-

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[4] Bowen and his coworkers were the first to consider the possibility that the equilibrium

$$Cr_2O_7^{--} + H_2O \rightleftharpoons 2HCrO_4^- \tag{19}$$
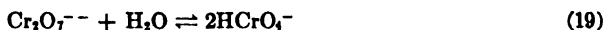
might be important in determining the mechanism of chromic acid oxidations. Unfortunately the work of Neuss and Rieman was not available to them; hence they chose for the equilibrium constant of reaction 19 a value which now appears to be in error.

sponds to the monomeric formula $C_5H_5NHCrOCl_4 \cdot H_2O$. Moreover these salts (e.g., Rb_2CrOCl_5) are isomorphous with the corresponding salts of pentavalent niobium (e.g., Rb_2NbOCl_5). Although these facts support the conclusion that these compounds contain pentavalent chromium, the low magnetic susceptibility (5) of the pyridinium salt implies that the compound contains only hexavalent chromium. No explanation of the discrepancy is at present available.

When the compound $C_5H_5NHCrOCl_4$ (or any other compound of the same series) is treated with water, it quickly disproportionates to give two compounds, one of trivalent and one of hexavalent chromium. But since the rate of this process is measurable (see below) the compound cannot initially contain chromium in these different valence states. Wagner (69) showed that Weinland's pyridinium salt of $CrOCl_4^-$ oxidized iodide in neutral or slightly acid solutions, whereas it is well known that ordinary dichromates do not. These facts are clearly consistent with the conclusion that $C_5H_5NHCrOCl_4$ is a compound of pentavalent chromium, and with the conclusion (cf. equation 33) that such pentavalent chromium compounds cause the induced oxidation of iodide in dilute acid solution.

The oxidizing properties of pentavalent chromium may be expected to vary considerably with the composition and structure of the particular pentavalent chromium intermediate present. Hence, the intermediate formed in a given chromic acid oxidation need not behave exactly like any of the oxychlorides just discussed. However, Wagner (69) in his investigations of the chromic acid oxidation of oxalic and lactic acids showed that in these reactions the intermediate formed does act very much like $C_5H_5NHCrOCl_4$. The latter compound oxidizes iodide ions in solutions containing far less acid than is required for the oxidation of iodide ions by compounds of hexavalent chromium. To demonstrate the similarity between this compound and the postulated pentavalent chromium intermediate, he neutralized a reaction mixture in which chromic acid had partially oxidized either lactic or oxalic acid, and then added an inorganic iodide to the mixture. Iodine was liberated under conditions of acidity where chromates alone do not oxidize iodide at all. Clearly, some metastable compound containing chromium in an intermediate valence state must be responsible for this action. In his most spectacular experiment, Wagner reduced the acidity of his reaction mixture with acetate ion and at the same time precipitated the unreacted hexavalent chromium as barium chromate. That is, he started with 30 cc. of a solution 0.17 N with respect to sulfuric acid, 0.067 N with respect to potassium dichromate, and containing a large excess of lactic acid. After the oxidation had proceeded 30 per cent to completion, he poured the solution with violent stirring into a large excess of barium acetate solution. Finally, to equal successive samples · of this mixture he added, at various times, an excess of a solution of potassium iodide. The amounts of iodine formed are shown in table 6. Evidently the intermediate (and probably pentavalent) chromium compound which constitutes an appreciable fraction (about 5 per cent) of the total chromium present, does not disappear instantaneously when the pH of the solution is about 5. Wagner also showed that, when the pH is about 7, the rate of disappearance is much greater.

Other compounds of pentavalent chromium have been reported, but their oxidizing properties are of relatively little interest in connection with the present study. The magnetic susceptibilities (66) of salts of perchromic acid (e.g., K_3CrO_8) show that these compounds must contain either pentavalent or heptavalent chromium; the former is much more probable. F. Hein (32) prepared a series of polyphenylated derivatives of chromium including $(C_6H_5)_5CrOH$, $(C_6H_5)_4CrI$, and $(C_6H_5)_3CrI \cdot (C_6H_5)_2O$. The magnetic susceptibilities (41) of these substances indicate that they all are compounds of pentavalent chromium. This valence is fairly evident for the compound $(C_6H_5)_4CrI$, but the others appear to be compounds of hexavalent or tetravalent chromium. Clearly the entire series needs further investigation.

Recently Wartenberg (71) has prepared both CrF_4 and $CrCl_4$; these are relatively stable and are unquestionably compounds of tetravalent chromium.

The dioxide is well known, but the magnetic susceptibility data (5) do not unambiguously distinguish between a true compound of tetravalent chromium

TABLE 6

Oxidation of iodide by transitory chromium compound

TIME BEFORE ADDITION OF KI	0.1 N $Na_2S_2O_3$ USED TO TITRATE IODINE
seconds	*cc.*
0	0.70
10	0.60
30	0.65
60	0.40
120	0.25
300	0.10

and a mixed oxide, $CrO_3 \cdot Cr_2O_3$. There are no data to exclude either one of these possibilities. Of somewhat more interest are the compounds which Étard (23) obtained by treating toluene (or related compounds) with chromyl chloride, CrO_2Cl_2. Where toluene is used, the reaction product contains two molecules of the chloride to one of the hydrocarbon, e.g., $C_6H_5CH_3 \cdot 2CrO_2Cl_2$. This compound, when hydrolyzed, decomposes to give benzaldehyde and compounds of both trivalent and hexavalent chromium:

$$3[C_6H_5CH_3 \cdot 2CrO_2Cl_2] \rightarrow 3C_6H_5CHO + 4CrCl_3 + 2H_2CrO_4 + H_2O \quad (49)$$
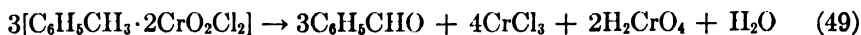
These hydrolysis products suggest for Étard's compounds structures like

$$C_6H_5C\underset{\displaystyle OCrCl_2OH}{\overset{\displaystyle OCrCl_2OH}{\overset{\displaystyle H}{\big<}}}$$
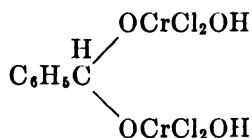
Such structures indicate that the compounds in question contain tetravalent chromium. No magnetic investigations of these substances have yet been made.

V. PROPERTIES OF TETRAVALENT AND PENTAVALENT CHROMIUM

The data so far presented can be used to make approximate estimates of the oxidizing powers of compounds containing pentavalent chromium. In each instance the exact potential must depend upon the particular compound of pentavalent chromium present, but the estimates given hereafter are so rough that such variations may be neglected.

The kinetics of the initial reaction between ferrous ion and a compound of hexavalent chromium show that the process is a reversible one, and that the equilibrium is displaced toward the starting materials.

$$Cr^6 + Fe^{++} \rightleftarrows Cr^5 + Fe^{+++} \tag{9}$$
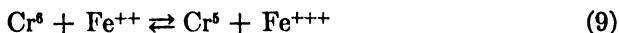
Since the equilibrium is displaced toward the left, the standard oxidation potential for the ferric ion–ferrous ion couple must exceed that for the Cr^6–Cr^5 couple. Therefore, since (46) for the reaction

$$Fe^{+++} + e \rightleftarrows Fe^{++} \tag{50}$$

the standard potential, E^0, is equal to 0.74 volt, for the reaction

$$Cr^6 + e \rightleftarrows Cr^5 \tag{51}$$

the standard potential must be $E \leq 0.62$ volt. That is to say, if the equilibrium 9 is displaced at least 99 per cent to the left, the difference between the standard potentials of reactions 50 and 51 must be at least 0.12 volt. The effect of hydrogen ions is here omitted; but since all the data under consideration have been obtained in the region between 0.001 and 1 M acid, this omission is unlikely to cause an error in potential of more than a few tenths of a volt, and most of this error cancels out when the figures here given are applied (uncorrected for H^+ effect) to a system other than the one from which the data were secured.

The assignment of a potential of 0.6 volt or less to the Cr^6–Cr^5 couple permits the assignment of a potential of 1.75 volt or more for the reaction:

$$Cr^5 + 2e \rightleftarrows Cr^3 \tag{52}$$

This conclusion follows from the fact that, for the reaction

$$7H^+ + HCrO_4^- + 3e \rightleftarrows Cr^3 + 4H_2O \tag{53}$$
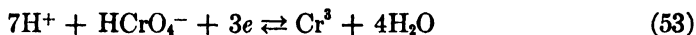
the potential (46), E^0, is 1.36 volt. Further, the conclusion would not be greatly modified if a moderately stable Cr^5–Cr^6 complex (see equation 42) exists.

The lower limit (1.75 volt) for the potential of the Cr^5–Cr^3 couple is consistent with the chromic acid oxidation of bromide induced by arsenite. This reaction very probably parallels the induced oxidation of iodide. It will later be shown that iodide is oxidized by pentavalent chromium to hypoiodite; hence bromide is presumably oxidized to hypobromite

$$Cr^5 + Br^- \rightarrow Cr^3 + BrO^- \tag{54}$$
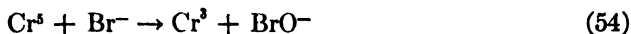
The potential for the Br^-–BrO^- couple is 1.6 volt. Clearly, then, the Cr^5–Cr^3 couple has sufficient potential to cause reaction 54.

Although it is thus possible to set a lower limit to the potential of the Cr^5–Cr^3 couple, it is not possible to assign a precise upper limit to this potential. A rough idea of this upper limit may be obtained by applying the theory of absolute reaction rates (25) to Benson's data (4). The argument is rather tenuous; it has, however, led the author to the opinion that the potential of the Cr^5-Cr^3 couple probably does not exceed 2 volts.

It has not proved possible to make even an approximate estimate of the potential for the reactions

$$Cr^5 + e \rightleftarrows Cr^4 \tag{55}$$

and

$$Cr^4 + e \rightleftarrows Cr^3 \tag{56}$$

To the second of these, a minimum potential of 1.5 volts may be assigned, on the basis of the quantitative oxidation of manganous ion to manganic ion (or MnO_2) by tetravalent chromium. But by how much the potential exceeds 1.5 volts is quite uncertain.

Stefanovskiĭ (82) attempted to measure the potentials involved in equations 55 or 56 directly. Although his experiments clearly reveal that compounds containing chromium in intermediate valence states have high oxidizing power, his data do not permit the exact determination of the potentials which he was seeking.

It should be noted that tetravalent chromium is not only a strong oxidizing agent but also (in all probability) a good reducing agent. Since the potential for reaction 56 is greater than 1.5 volts, the potential for the reaction

$$Cr^6 + 2e \rightleftarrows Cr^4 \tag{57}$$
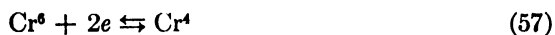
cannot exceed 1.3 volts; it may, however, be much less than 1.3 volts, and if such is the fact, then tetravalent chromium can be oxidized with moderate ease.

Finally, it is necessary to present the argument that pentavalent chromium oxidizes iodide to hypoiodite rather than to iodine. First, it should be noted that the direct oxidation of iodide to iodine requires the formation of iodine atoms:

$$Cr^5 + I^- \rightarrow Cr^4 + I^0 \tag{58}$$

and

$$Cr^4 + I^- \rightarrow Cr^3 + I^0 \tag{59}$$

But the assumption that these reactions occur involves an internal contradiction. In a reaction such as the oxidation of arsenite, tetravalent chromium is first produced (see equation 32a). In order to explain the observed induction factor of 2, it is necessary to assume that this tetravalent chromium is converted quantitatively (by direct or indirect reaction with hexavalent chromium) to pentavalent chromium. Hence the tetravalent chromium cannot react with iodide. On the other hand, in order that iodine be produced in reaction 59 (also a necessary requisite for the induction factor of 2) the compound containing

tetravalent chromium must react quantitatively with iodide, and may not react either directly or indirectly with a compound of hexavalent chromium. In view of this internal contradiction, it must be concluded that pentavalent chromium oxidizes iodide to something other than iodine atoms—most probably to hypo-iodite ions. The analogous conclusion can be reached (with high probability if not with certainty) by considering the potentials involved in the induced oxidation of bromide to bromine by way of bromine atoms.

<div align="center">VI. REFERENCES</div>

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THE KETENE ACETALS

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CONTENTS

I. INTRODUCTION AND HISTORICAL

Ketene acetals have the general structure I, which represents an ether of the enolic form (II) of an ester. The name of this class of compounds, however, is derived from the fact that they bear the same structural relationship to the ketenes (III) that acetals bear to aldehydes and ketones.

$$R'R''C=C \begin{cases} OR \\ OR \end{cases} \qquad R'R''C=C \begin{cases} OH \\ OR \end{cases} \qquad R'R''C=C=O$$

$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$
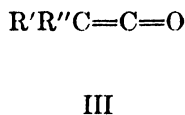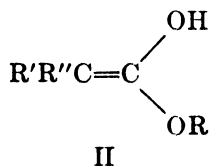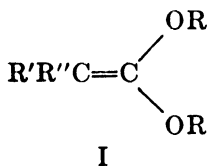
The first compound of structure I to appear in the literature was reported by Biginelli (6) in 1891 as the diphenyl ether of vinylidene glycol. This structure was assigned to the product obtained from the reaction of an alkaline solution of phenol with methylchloroform and its formation was postulated as shown in reaction 1:

$$CH_3CCl_3 + 2C_6H_5OK + KOH \rightarrow CH_2=C(OC_6H_5)_2 + 3KCl + H_2O \qquad (1)$$

Biginelli's compound melted at 95–96°C. At about the same time Heiber (11) reported the product of this reaction to be triphenyl orthoacetate, $CH_3C(OC_6H_5)_3$,

m.p. 97–97.5°C. This contradiction remained in the literature, although later workers (45, 50) accepted Biginelli's structure, until Cope (8) presented convincing evidence that neither Biginelli nor Heiber had the compound he reported, but that both had isolated the diphenyl ether of ethylene glycol, m.p. 95–97°C. This product was presumed by Cope to have been formed from ethylene chloride, a contaminant of the methylchloroform used by the earlier workers. The preparation (reaction 8) and properties of ketene diphenylacetal, which are described subsequently, substantiate Cope's conclusion regarding the products reported by Biginelli and Heiber.

The first authentic ketene acetal was described by Reitter and Weindell (39) in 1907 as β-diethoxyacrylic ester (VI). They obtained this compound rather than the expected malonic ester orthoester (V) as the alcoholysis product of the iminoester (IV) derived from cyanoacetic ester (reaction 2). There is no doubt now that the orthoester V was the precursor of the carbethoxyketene diethylacetal obtained in this work. Reitter and Weindell noted the acetal structure of VI and the similarity of its reactions to those of the previously described ketene (48).

$$C_2H_5OOCCH_2CN \xrightarrow[HCl]{C_2H_5OH} C_2H_5OOCCH_2C(OC_2H_5)=NH \cdot HCl \xrightarrow{C_2H_5OH}$$
$$IV$$

$$NH_4Cl + C_2H_5OOCCH_2(OC_2H_5)_3 \rightarrow C_2H_5OH +$$
$$V$$

$$C_2H_5OOCCH=C(OC_2H_5)_2 \quad (2)$$
$$VI$$
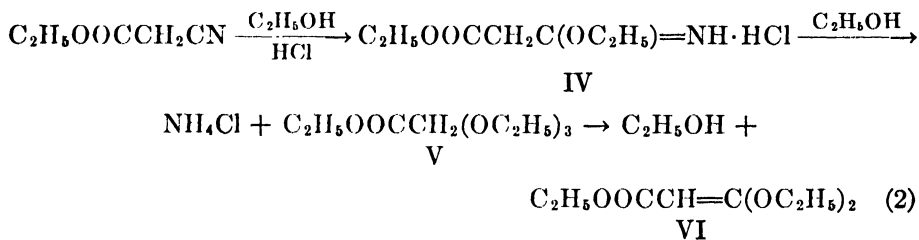
In 1922 Staudinger and Rathsam (50) attached the name "ketene acetals" to this class of compounds when they described the preparation and properties of phenylketene diethylacetal (VII). This compound was obtained by the pyrolysis of ethyl orthophenylacetate:

$$C_6H_5CH_2C(OC_2H_5)_3 \rightarrow C_2H_5OH + C_6H_5CH=C(OC_2H_5)_2 \quad (3)$$
$$VII$$
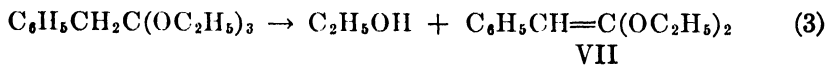
Attempts to extend this method to the preparation of ketene acetals from orthoacetic and orthopropionic esters were unsuccessful. These esters when heated alone or with phosphorus pentoxide were reported to pyrolyze to the normal esters, ethyl acetate and ethyl propionate, and ether. It was concluded, therefore, that an orthoester must contain an activated α-hydrogen to undergo the type of pyrolysis shown in reaction 3 (50).

At about the same time as Staudinger and Rathsam described the preparation of VII, Scheibler and Ziegner (45) reported the isolation of the parent compound, ketene diethylacetal, as a minor reaction product from certain acetoacetic ester condensations involving ethyl acetate. Later Scheibler and coworkers (44) described detailed procedures for the preparation of this and other homologous ketene acetals. Essentially, Scheibler's method consisted in decomposition by water of a "primary reaction product," represented in reaction 4 as the addition

compound of ethyl acetate to the sodium enolate of this ester, to form sodium acetate and ketene diethylacetal:

$$CH_3COOC_2H_5 + Na \text{ (or } C_2H_5ONa) \rightarrow CH_2=C\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{\Big\langle}} \xrightarrow{CH_3COOC_2H_5}$$

$$CH_3COCH_2C\overset{\displaystyle ONa}{\underset{\displaystyle OC_2H_5}{\Big\langle}}OC_2H_5 \xrightarrow{H_2O} CH_3COONa + CH_2=C(OC_2H_5)_2 \quad (4)$$
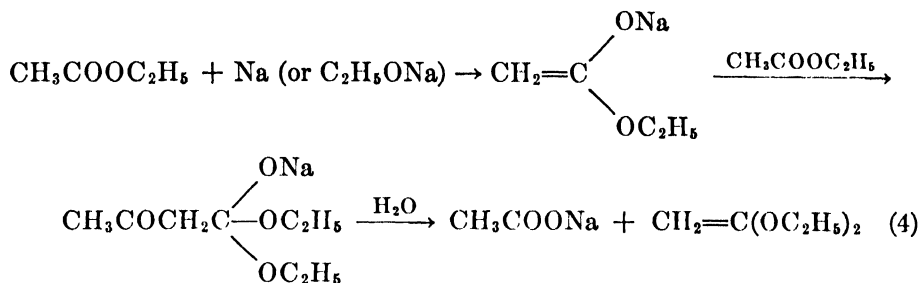
It was the failure of other investigators (47) to repeat the work reported from Scheibler's laboratory that led to the expansion of the field of the ketene acetals that is discussed in the subsequent sections of this review.

In one instance a ketene acetal has been prepared directly from an ester (1). The action of diazomethane on tricarbomethoxymethane yielded dicarbomethoxyketene dimethylacetal (VIII) in 47 per cent yield; a 17 per cent yield of the C-methylated product, tricarbomethoxyethane, which results from the rearrangement of VIII, also was obtained (reaction 5). The success of this reaction is due to the strong enolic character of tricarbomethoxymethane. Staudinger and Meyer (49) had investigated the alkylation of the potassium enolate of methyl diphenylacetate and found that only C-alkylation occurred; a similar result was obtained with the sodium enolate of ethyl diphenylacetate resulting from the decarbethoxylation of diphenylmalonic ester (9).

$$(CH_3OOC)_2C=C(OH)OCH_3 + CH_2N_2 \rightarrow$$

$$N_2 + (CH_3OOC)_2C=C(OCH_3)_2 \rightarrow (CH_3OOC)_2C(CH_3)COOCH_3 \quad (5)$$

$$\text{VIII}$$

Staudinger and Rathsam (50) attempted the preparation of diphenylketene diethylacetal by the reaction of diphenylketene with orthoformic ester, but found that the ester added to the ketene to produce diphenylcarbethoxyacetaldehyde diethylacetal in the following manner:

$$(C_6H_5)_2C=C=O + HC(OC_2H_5)_3 \rightarrow (C_6H_5)_2C(COOC_2H_5)CH(OC_2H_5)_2 \quad (6)$$
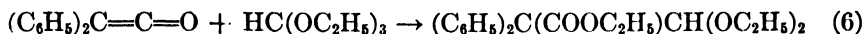
II. THE PREPARATION OF KETENE ACETALS

A. DEHYDROHALOGENATION OF α-BROMOACETALS

When it became obvious that the procedures described by Scheibler and coworkers (44, 45) could not be duplicated (47), the preparation of ketene diethylacetal by other procedures was undertaken. An obvious approach to this ketene acetal was the dehydrohalogenation of a haloacetal (IX). When this reaction was applied to iodoacetal (IX: X is iodine) with potassium t-butoxide in t-butyl alcohol as the dehydrohalogenating agent, ketene diethylacetal (X) was obtained in 52 per cent yield (3).

$$XCH_2CH(OC_2H_5)_2 + t\text{-}C_4H_9OK \rightarrow$$
$$\text{IX}$$

$$CH_2{=}C(OC_2H_5)_2 + KI + t\text{-}C_4H_9OH \quad (7)$$
$$\text{X}$$
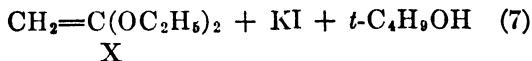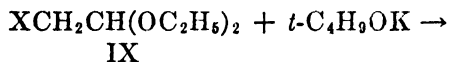
The use of a tertiary alcohol as a medium for this dehydrohalogenation is essential because of the tendency of primary and secondary alcohols to add to the ketene acetal to produce orthoesters (reaction 28). In this connection it is of interest to note that potassium hydroxide in ethyl alcohol gives 95 per cent of the replacement reaction product, the acetal of glycolic aldehyde ($HOCH_2CH(OC_2H_5)_2$), when the halogen of IX is chlorine; the corresponding bromo- and iodo-acetals give, respectively, 70 per cent and 30 per cent yields of the replacement product with this reagent. The remainder of the iodoacetal in the latter case is converted to ethyl acetate and ethyl orthoacetate, further reaction products of the initially formed ketene acetal X (3). Later it was found (12, 25) that ketene diethylacetal could be prepared in equally good yields using the bromoacetal instead of the iodoacetal in reaction 7.

Ketene diethylacetal, as obtained from reaction 7, is a colorless liquid that boils at 124–126°C. It reacts rapidly and exothermically with water and alcohol at room temperature to form, respectively, ethyl acetate and ethyl orthoacetate (reactions 26 and 28), and it is hydrogenated over Raney nickel to acetaldehyde diethylacetal (reaction 40) (3). In contrast to these properties the product described by Scheibler (44, 45) boiled at 77–78°C. and was isolated from an aqueous reaction mixture.

The extension of reaction 7 to other haloacetals has led to the preparation of the chloro- and bromo-ketene acetals (XI) (5, 35); the dichloro- and dibromo-ketene acetals (XII) (35); ketene di-n-propyl-, diisobutyl-, and diisoamyl-acetals (XIII) (33); phenylketene dimethylacetal (XIV) (19); and a variety of methylenedioxolanes and methylenedioxanes (XV) (19). Related to these latter groups of cyclic acetals is the ketene acetal of cis-1,2-cyclohexanediol (XVI), which has been prepared by Winstein (53) by the procedure of reaction 7. In the case of XIV the product prepared from the bromoacetal by reaction 7 is of considerably higher purity than that resulting from the pyrolysis of the cor-

$$XCH{=}C(OC_2H_5)_2 \qquad X_2C{=}C(OC_2H_5)_2 \qquad CH_2{=}C(OR)_2$$
$$\text{XI} \qquad\qquad\qquad \text{XII} \qquad\qquad\qquad \text{XIII}$$

$$C_6H_5CH{=}C(OCH_3)_2 \qquad RR'C{=}CO(CH_2)_nO$$
$$\text{XIV} \qquad\qquad\qquad \text{XV}$$

$$CH_2{=}C\underset{\displaystyle \text{O-C-H}}{\overset{\displaystyle \text{O-C-H}}{}}$$

XVI
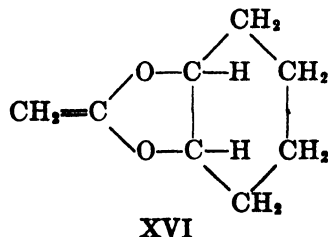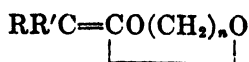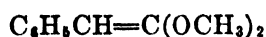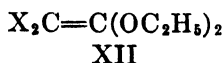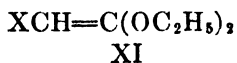
(R is H, Cl, Br, or C_6H_5;
R' is H or Cl; n is 2 or 3)

responding orthoester (reactions 3 and 13). The yields of the ketene acetals XI–XV from reaction 7 are 50–85 per cent of the theoretical.

The application of reaction 7 to bromoacetaldehyde diallyl- and dibenzyl-acetals yields the esters allyl allylacetate, CH_2=$CHCH_2CH_2COOCH_2CH$=CH_2, and benzyl o-tolylacetate, o-$CH_3C_6H_4CH_2COOCH_2C_6H_5$, in 43 per cent and 46 per cent yields, respectively (14). These products result from the rearrangement of one of the R groups of these ketene acetals (XIII: R is allyl or benzyl) as they are formed from the dehydrohalogenation of the bromoacetals (cf. the rearrangement of XXXVI in reaction 16).

The dehydrohalogenation of bromoacetaldehyde diphenylacetal (reaction 8) has been used to prepare ketene diphenylacetal (XVII), which Biginelli (6) reported to have been produced in reaction 1; triphenyl orthoacetate, which Heiber (11) reported to result from reaction 1, was prepared from this ketene acetal by the addition of phenol as shown in reaction 30 (21).

$$BrCH_2CH(OC_6H_5)_2 \xrightarrow{\textit{t-}C_4H_9OK} CH_2=C(OC_6H_5)_2 \qquad (8)$$
$$XVII$$
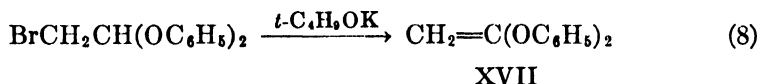
As the properties of XVII, a liquid boiling at 115–116°C. (1 mm.), and triphenyl orthoacetate, m.p. 61–62°C., do not agree with those reported by Biginelli and Heiber for the compounds they obtained from reaction 1, Cope's conclusion that each of these investigators had isolated the diphenyl ether of ethylene glycol, m.p. 95–97°C., is substantiated.

It is possible to prepare chloro- and bromo-ketene diethylacetals (XI) from the corresponding dihaloacetals using sodium ethoxide in ethyl alcohol solution instead of potassium t-butoxide in t-butyl alcohol, the dehydrohalogenating agent of reaction 7. This is because the haloketene acetals (XI) react sufficiently slowly with ethyl alcohol in the presence of alkali to permit their isolation (34). However, these ketene acetals may not be allowed to remain too long in this medium as they are slowly transformed to the ethyl orthohaloacetates, $XCH_2C(OC_2H_5)_3$ (reaction 28). This type of reaction product was erroneously described as the isomeric ethoxybromoacetal, $C_2H_5OCHBrCH(OC_2H_5)_2$, in an earlier investigation of the reaction of dibromoacetal with sodium ethoxide (5).

Reaction 7 is not applicable to the preparation of alkylketene acetals. When such bromoacetals as XVIII, XIX, and XX are dehydrohalogenated with potassium t-butoxide, the acetals of the corresponding α,β-unsaturated aldehydes (XXI), rather than the ketene acetals, are produced as shown in reaction 9. The kinetics of this reaction show it to be second order and this, together with the fact that the isopropylketene acetal (obtained from reaction 10) which would result from the alternative dehydrohalogenation of XX is stable to the conditions of the reaction, indicates that the mechanism of reaction 9 involves the initial removal of the β-proton by the base followed by expulsion of the bromide anion (17).

The exclusive removal of the β-proton of XX in this dehydrohalogenation shows that the inductive effects of the methyl and ethoxyl groups do not control

$$(CH_3)_2CBrCH(OC_2H_5)_2 \qquad CH_3CH_2CHBrCH(OC_2H_5)_2$$
$$\text{XVIII} \qquad\qquad\qquad \text{XIX}$$

$$(CH_3)_2CHCHBrCH(OC_2H_5)_2 \xrightarrow{t\text{-}C_4H_9OK} (CH_3)_2C{=}CHCH(OC_2H_5)_2 \quad (9)$$
$$\text{XX} \qquad\qquad\qquad\qquad \text{XXI}$$

the course of the reaction, because the greater effect of the latter groups should facilitate the removal of the proton of the acetal group—obviously the more acidic hydrogen of the two available for dehydrohalogenation in XXa—with the resultant formation of the ketene acetal. It must be concluded, therefore, that the ethoxyl groups function in resonance structures such as XXb, which promote the separation of the hydrogen of the acetal group as a hydride anion rather than as a proton, and thereby permit a structure such as XXc to react with the base to produce XXI.

If oxygen could expand its valence shell as sulfur appears to do in CVIIIa of reaction 60 and permit the hydrogen of the acetal group to resonate as a proton, it might be possible to prepare an alkylketene acetal from such a bromoacetal as XX.

B. REACTION OF SODIUM WITH α-BROMOÖRTHOESTERS

Alkylketene acetals (XXIII) may be prepared by the removal of the elements of an alkyl hypobromite from an α-bromoörthoester (XXII) with metallic sodium as shown in reaction 10.

$$RCHBrC(OC_2H_5)_3 + 2Na \rightarrow RCH{=}C(OC_2H_5)_2 + NaBr + C_2H_5ONa \quad (10)$$
$$\text{XXII} \qquad\qquad\qquad \text{XXIII}$$
(R is H or alkyl)

In this manner ketene, methylketene (52), n-propylketene, and isopropyl-ketene diethylacetals (17) as well as ketene dimethylacetal (14) have been prepared in 60–80 per cent yields. This is the most general method of preparing ketene acetals, as there is no alternative position in which the double bond may form as there is in the bromoacetal of reaction 9. Ketene acetals prepared by reaction 10 have been found to be quite stable under the conditions of reaction

9 and thereby are shown not to be intermediates in the dehydrohalogenation of the acetals of α-bromoaldehydes to the acetals of α,β-unsaturated aldehydes (17, 42).

The application of reaction 10 to the preparation of dialkylketene acetals, $(R_2C{=}C(OR')_2)$, has not been made because it has not been possible as yet to prepare the requisite haloörthoesters, $R_2CXC(OR')_3$ (13). Surprisingly, reaction 10 cannot be used to prepare phenylketene dimethylacetal (XIV); a complex sodium salt of the ester moiety and sodium bromide are the products obtained from the reaction of sodium with trimethyl orthophenylbromoacetate (31).

When α-haloörthoacetic esters are treated with zinc or magnesium, polymeric reaction products instead of ketene acetals are obtained (4). Such products indicate that these metals remove the elements of the alkyl hypohalite intermolecularly from the haloörthoester rather than in the intramolecular manner of reaction 10. This behavior of α-haloörthoesters is in marked contrast to the facile intramolecular removal of the elements of an alkyl hypohalite from a β-haloether by zinc in the Boord method of preparation of olefins (7).

C. PYROLYSIS OF ORTHOESTERS

It was by this procedure that the ketene acetals (VI and VII) described in the earlier literature were prepared (reactions 2 and 3). Although Reitter and Weindell (39) did not isolate the intermediate orthoester (V), they assumed it to be an intermediate in the formation of VI. A study of the preparation of methyl orthocyanoacetate (XXIV) has shown that such negatively substituted orthoesters may be isolated if all traces of acid are removed prior to their distillation (29). Acids catalyze the pyrolysis of the orthoester to the ketene acetal (XXV) as they do the reverse reaction, the addition of the alcohol to the acetal to produce the orthoester (30):

$$CNCH_2C(OCH_3)_3 \underset{\longleftarrow}{\overset{H^+}{\longrightarrow}} CNCH{=}C(OCH_3)_2 + CH_3OH \qquad (11)$$
$$\text{XXIV} \qquad\qquad\qquad \text{XXV}$$
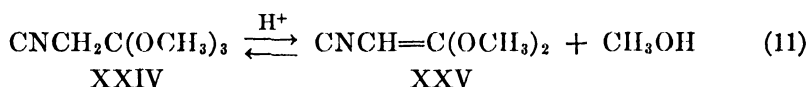
Reaction 11 proceeds to the right when the orthoester is heated and the alcohol removed by distillation; the orthoester is formed from its components at room temperature, but can be isolated by distillation only after the removal of the last traces of the acid catalyst with alkali (30). By following this procedure such orthoesters as V and XXIV may be isolated in the pure state in 62–82 per cent yields (29) and then smoothly pyrolyzed to the ketene acetals (30).

The pyrolysis of ethyl orthophenylacetate (reaction 3) gives the corresponding ketene acetal (VII) in approximately 70 per cent yield when the orthoester is slowly distilled as in a fractional distillation (31). Accompanying this product, however, is a 20 per cent yield of ethyl phenylacetate (XXVI), together with ethylene and a small amount of meso-diethyl α,α'-diphenylsuccinate, which Staudinger and Rathsam (50) isolated but did not identify (see reaction 53 for the formation of the homologous methyl ester). The formation of ethyl phenylacetate (XXVI) during this pyrolysis doubtless is the result of further

decomposition of the ketene acetal (reaction 12), as the evolution of ethylene is not brisk until the evolution of ethyl alcohol (reaction 3) is nearly complete. Also, each redistillation of the ketene acetal VII usually produces a small amount of XXVI.

$$C_6H_5CH{=}C(OC_2H_5)_2 \longrightarrow C_6H_5CH_2COOC_2H_5 + CH_2{=}CH_2 \quad (12)$$
$$\text{VII} \qquad\qquad\qquad \text{XXVI}$$
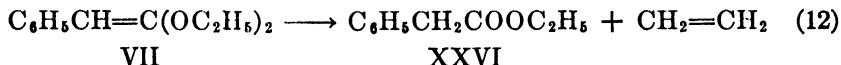
As phenylketene *dimethyl*acetal (XXIX) cannot follow reaction 12, it would be expected that the pyrolysis of methyl orthophenylacetate (XXVII) would produce XXIX and none of the normal ester (XXXII). However, this is not the case; the methyl orthoester (XXVII) gives higher yields (33 per cent) of the normal ester (XXXII) and lower yields (59 per cent) of the ketene acetal (XXIX) than does ethyl orthophenylacetate. The methyl orthoester is much more stable than the ethyl ester to pyrolysis, but when heated to 250–260°C. a vigorous evolution of methyl alcohol occurs. However, only 40–50 per cent of the amount of alcohol expected on the basis of reaction 3 distils from the orthoester during this initial rapid pyrolysis, which subsides within 15 min. Thereafter the evolution of the alcohol is quite slow and incomplete. The amount of alcohol obtained, together with the distillation behavior of the product, led to the postulation of the reaction course shown in reaction 13 for this pyrolysis.

$$2C_6H_5CH_2C(OCH_3)_3 \longrightarrow CH_3OH +
\left[\begin{array}{c}
H \quad C(OCH_3)_2 \\
C_6H_5CH \quad CHC_6H_5 \\
CH_3O-C(OCH_3)_2
\end{array} \right] \longrightarrow$$
$$\text{XXVII} \qquad\qquad\qquad\qquad \text{XXVIII}$$

$$C_6H_5CH{=}C(OCH_3)_2 + \left[\begin{array}{c} C_6H_5CHCH(OCH_3)_2 \\ | \\ OCH_3 \end{array} \right] \longrightarrow$$
$$\text{XXIX} \qquad\qquad\qquad \text{XXX}$$

$$(CH_3)_2O + \left[\begin{array}{c} C_6H_5CH{-}CHOCH_3 \\ \diagdown \diagup \\ O \end{array} \right] \longrightarrow C_6H_5CH_2COOCH_3 \quad (13)$$
$$\text{XXXI} \qquad\qquad\qquad \text{XXXII}$$
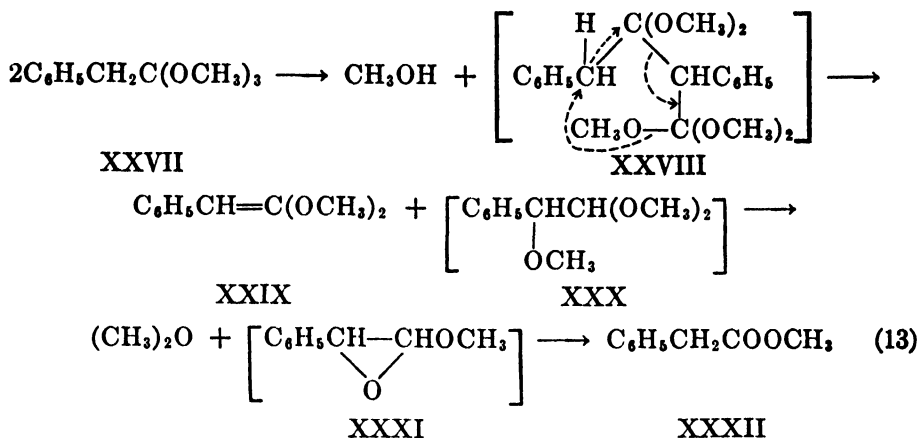
The formation of the intermediate XXVIII from two equivalents of XXVII seems necessary to account for the following observations on this pyrolysis: (a) no more than one-half of the expected alcohol is obtained readily from the orthoester, (b) rapid distillation of the pyrolysis product gives a mixture (XXIX and XXX) boiling in the range of the original orthoester and having a methoxyl content intermediate between that of the orthoester and that of the ketene acetal, and (c) fractional distillation of the mixture from (b) is accompanied by marked fluctuations in the boiling point (transformation of XXX *via* XXXI to XXXII) before the final separation of the major reaction products, XXIX and XXXII (31).

This unusual pyrolysis behavior of the orthoester XXVII is in marked contrast to its behavior when pyrolyzed in the presence of one equivalent of the ketene acetal XXIX. In this case *all* the alcohol required for the conversion of the orthoester to the ketene acetal is evolved rapidly; 88 per cent of the ketene acetal, but *no methyl phenylacetate*, is obtained as the pyrolysis product. This behavior leads to the conclusion that the ketene acetal (XXIX) reacts with the orthoester (XXVII) with the elimination of alcohol to produce an intermediate, e.g., XXXIII, which then pyrolyzes to two moles of XXIX, as indicated in reaction 14 (31).

$$XXIX + XXVII \longrightarrow$$

$$CH_3OH + \left[\begin{array}{c} OCH_3 \\ | \\ C_6H_5CH{=}CCHC(OCH_3)_3 \\ | \\ C_6H_5 \end{array} \right] \longrightarrow 2XXIX \quad (14)$$

XXXIII
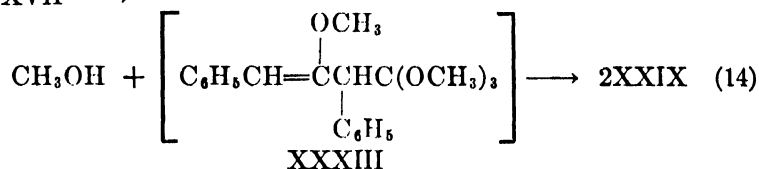
Phenylketene dimethylacetal prepared by reaction 13 is a yellow liquid, which has a decidedly lower refractive index (see No. 14, table 1) than that of the colorless product obtained from the dehydrohalogenation of phenylbromoacetaldehyde dimethylacetal by reaction 7.

Although Staudinger and Rathsam (50) reported that such orthoesters as ethyl orthoacetate and ethyl orthopropionate pyrolyze to the normal ester and diethyl ether, a later study indicates that ethyl orthoacetate is converted to ethyl acetate, ethyl alcohol, and ethylene when heated at 200°C. for 24 hr. (14). Inasmuch as ketene diethylacetal undergoes pyrolysis to ethyl acetate and ethylene (reaction 15a) under the same conditions. it seemed that the ketene acetal might be an intermediate in the pyrolysis of the orthoester. This was shown to be the case when ethyl orthoacetate was pyrolyzed in the presence of phenol, which reacts with the ketene acetal as rapidly as it is formed, and before it can pyrolyze, to convert it *via* the intermediate XXXIV to ethyl acetate and phenetole (reaction 15).

$$CH_3C(OC_2H_5)_3 \xrightarrow{200°C.} C_2H_5OH + CH_2{=}C(OC_2H_5)_2 \xrightarrow{C_6H_5OH}$$

$$CH_3C{\overset{OC_2H_5}{\underset{OC_6H_5}{<}}} \longrightarrow CH_3COOC_2H_5 + C_6H_5OC_2H_5 \quad (15)$$

XXXIV

$$CH_2{=}C(OC_2H_5)_2 \longrightarrow CH_3COOC_2H_5 + C_2H_4 \quad (15a)$$
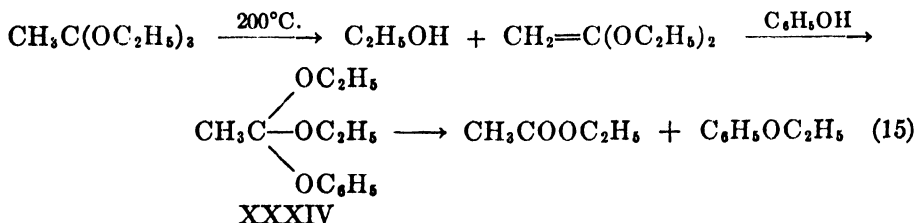
When this pyrolysis procedure was extended to a variety of simple and mixed orthoacetic esters, all appeared to follow the reaction course illustrated in reaction 15. It is possible to rationalize the products of this reaction without the intermediate formation of the ketene acetal, i.e., by the phenol reacting

directly with the orthoester to give alcohol and XXXIV, which then would pyrolyze to the products that are isolated. Such a reaction course, however, seems unlikely for the following reasons: (a) no phenyl acetate, which could result from an ester interchange between phenol and the reaction product ethyl acetate, is present after the pyrolysis and (b) the product of the pyrolysis of diethyl benzyl orthoacetate (XXXV) in the absence of phenol is ethyl o-tolyl-acetate (XXXVII), which can be formed only as shown in reaction 16 by the rearrangement of the intermediate ketene acetal (XXXVI) (14):

$$
\underset{\text{XXXV}}{\overset{\displaystyle OC_2H_5}{\underset{\displaystyle OCH_2C_6H_5}{CH_3C{-}OC_2H_5}}} \longrightarrow C_2H_5OH + \left[\underset{\text{XXXVI}}{\overset{\displaystyle OC_2H_5}{\underset{\displaystyle OCH_2C_6H_5}{CH_2{=}C}}}\right] \longrightarrow
$$

$$
\underset{\text{XXXVII}}{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2COOC_2H_5}{\bigcirc}}} \tag{16}
$$
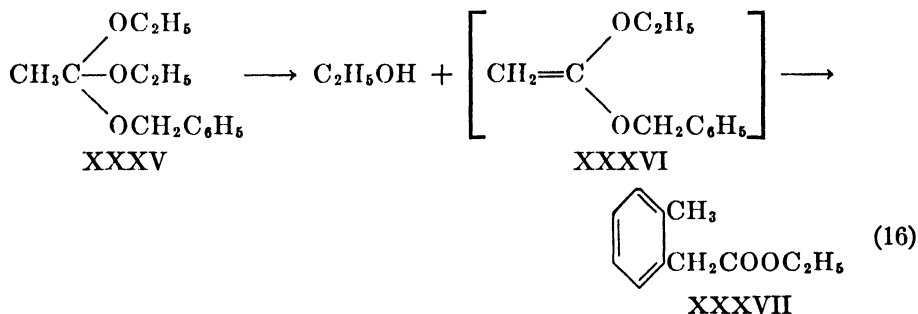
The orthoesters of bromo- and dibromo-acetic acids undergo two types of pyrolysis (14). One of these follows the course of reaction 15 to produce the alcohol, the normal ester, and ethylene. The other type of pyrolysis involves the loss of the elements of ethyl hypobromite to produce an ester containing one less bromine than the original orthoester (reaction 17). Further reaction of the ethyl hypobromite yields the secondary products, acetaldehyde and ethyl bromide, that are obtained from this pyrolysis.

$$
Br_2CHC(OC_2H_5)_3 \rightarrow C_2H_5OBr + BrCH{=}C(OC_2H_5)_2
$$
$$
\rightarrow BrCH_2COOC_2H_5 + C_2H_4 \tag{17}
$$

$$
CH_3CH_2OBr \longrightarrow CH_3CHO + HBr \xrightarrow{\ C_2H_5OH\ } C_2H_5Br + H_2O
$$
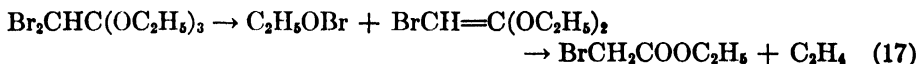
From the behavior of the orthoesters illustrated in reactions 2, 3, 11, 13, 15, 16, and 17 it is evident that pyrolysis to ketene acetals is a quite general reaction. If the orthoester does not have a negative α-substituent such as the phenyl, carbethoxy, or cyano group, the temperature necessary for its pyrolysis also causes the pyrolysis of the resulting ketene diethylacetal to ethylene and the normal ester. To date, neither the pyrolysis of methyl orthoesters without a negative α-substituent nor the pyrolysis of simple aliphatic orthoesters with secondary and tertiary α-carbons have been studied. However, it has been shown that ethyl orthobenzoate, which has no α-hydrogen, pyrolyzes to the normal ester and diethyl ether (14):

$$
C_6H_5C(OC_2H_5)_3 \rightarrow C_6H_5COOC_2H_5 + (C_2H_5)_2O \tag{18}
$$

D. REACTION OF STRONG BASES WITH ORTHOESTERS

The scope and generality of this method of preparation of ketene acetals are now under investigation in the Wisconsin Laboratory. To date only one report

of its use appears in the literature (16). This involves the preparation of tetraeth-oxyethylene, diethoxyketene diethylacetal (XL), by the action of sodium ethyl on pentaethoxyethane (XXXVIII) as illustrated in reaction 19.

$$(C_2H_5O)_2CHC(OC_2H_5)_3 + \overset{+}{Na}\overset{-}{C_2H_5} \longrightarrow$$
$$XXXVIII$$

$$C_2H_6 + (C_2H_5O)_2\overset{-}{C}C(OC_2H_5)_3\overset{+}{Na} \longrightarrow$$
$$XXXIX$$

$$(C_2H_5O)_2C{=}C(OC_2H_5)_2 + C_2H_5ONa \quad (19)$$
$$XL$$
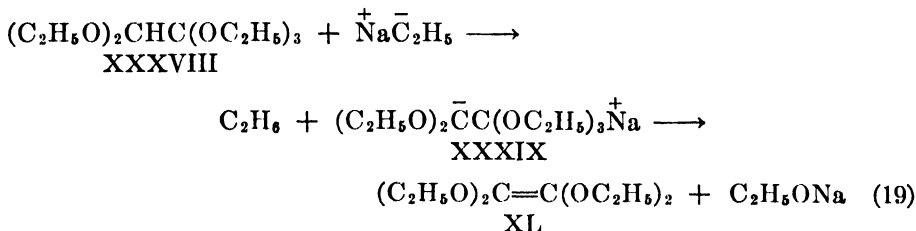
As shown, reaction 19 is a simple acid–base reaction in which a strong base, the ethyl anion, extracts a proton from the ortho ester to form ethane and the carbanion XXXIX, which then by elimination of an ethoxyl anion passes into the ketene acetal XL. The reaction, however, is much more complex than shown, as yields of 39 per cent of XL, 160 per cent of ethane, and 235 per cent of sodium ethoxide, based on the amount of the orthoester XXXVIII used in the reaction, are obtained. Nevertheless, this reaction appears to be the only one feasible for the preparation of the ketene acetal XL, as the orthoester is quite stable to heat; in fact it may be refluxed (b.p. 205–207°C.) for several hours without evidence of decomposition. Diethoxyketene diethylacetal (XL) is of particular interest because it previously has been reported (43) to dissociate spontaneously into the divalent carbon compound, carbon monoxide diethylacetal, $C(OC_2H_5)_2$, b.p. 78°C. The ketene acetal obtained from reaction 19 is a stable, colorless liquid, which boils at 195–196°C. with no evidence of decomposition or dis-sociation.

E. PREPARATION OF ORTHOESTERS

As orthoesters are required for three of the four methods by which ketene acetals are obtained, a few remarks on the preparation of certain members of this class of compounds seem appropriate. An excellent monograph covering the literature on the orthoesters to 1943 has been prepared by Post (38). The follow-ing discussion is limited to the observations made on the preparations of those orthoesters that have been studied in connection with the ketene acetals.

The most general and widely used method of preparation of orthoesters is that originated by Pinner (37), which involves the alcoholysis of an iminoester hydrochloride (XLI) obtained from the reaction of alcoholic hydrogen chloride with a nitrile (reaction 20). A study of the optimum conditions for this alco-holysis showed that 60–78 per cent yields of the ethyl esters of the normal-chain aliphatic orthoacids may be obtained; however, the alcoholysis of branched-chain iminoester hydrochlorides (XLI: R is isopropyl or isobutyl) gives only 20–30 per cent yields of the corresponding orthoesters (28). Accompanying the alcoholysis reaction is a competitive decomposition of the iminoester hydro-chloride to the amide (reaction 21). In certain alcoholyses a substantial yield of the normal ester also is obtained. The origin of this latter product is not too

clear; in certain cases (16) it appears to result from the decomposition of the orthoester into the normal ester and ether (reaction 22) under the catalytic influence of the iminoester hydrochloride (XLI); in other cases it appears that this salt is sufficiently acidic to cleave the orthoester formed in reaction 20 according to reaction 23 (29, 51).

$$RCN + C_2H_5OH + HCl \longrightarrow$$

$$\underset{XLI}{RC\overset{\displaystyle OC_2H_5}{=}NH \cdot HCl} \xrightarrow{\;C_2H_5OH\;} RC(OC_2H_5)_3 + NH_4Cl \quad (20)$$

$$\underset{XLI}{RC\overset{\displaystyle OC_2H_5}{=}NH \cdot HCl} \longrightarrow RCONH_2 + C_2H_5Cl \quad (21)$$

$$RC(OC_2H_5)_3 \xrightarrow{\;XLI\;} RCOOC_2H_5 + (C_2H_5)_2O \quad (22)$$

$$RC(OC_2H_5)_3 + XLI \longrightarrow$$
$$RCOOC_2H_5 + RC(OC_2H_5)=NH + C_2H_5Cl + C_2H_5OH \quad (23)$$
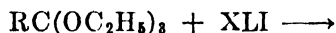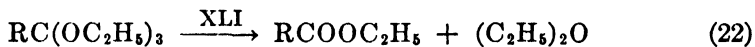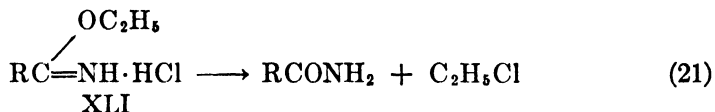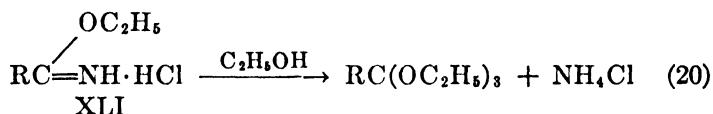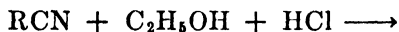
Some of reaction 21 always occurs even under the most favorable conditions that have been found for reaction 20 (28). When the R of XLI has a disubstituted α-carbon and particularly if this carbon has a halogen substituent, the amide of reaction 21 is the major if not the sole reaction product (22). For this reason the α-bromoörthoesters used for the preparation of ketene acetals by procedure B are prepared by the bromination of the orthoesters. This bromination proceeds satisfactorily in the presence of pyridine with esters of orthoacetic acid and its higher homologs, in which the α-carbon is secondary (4, 17, 28, 52). However, if the α-carbon is tertiary as in esters of orthoisobutyric acid, $(CH_3)_2CHC(OR)_3$, it has not been possible to effect such an α-bromination with a wide variety of brominating agents (13).

A case in which reaction 22 appears together with reaction 21 as a competing reaction is in the preparation of pentaethoxyethane, the orthoester (XXXVIII) used in reaction 19, from the alcoholysis of XLI (R is $(C_2H_5O)_2CH$). Under the optimum conditions found only a 12 per cent yield of this orthoester could be obtained from reaction 20; the major reaction products were the amide from reaction 21 and the ester together with some diethyl ether from reaction 22; a small (8 per cent) yield of the nitrile, $(C_2H_5O)_2CHCN$, possibly formed from the decomposition of the iminoester of reaction 23, also is obtained (16).

It is probable that reaction 23 is responsible for some of the normal ester that is often found among the products of the alcoholysis of iminoester salts. Orthoesters are very susceptible to cleavage by acids and it is likely that the iminoester hydrochlorides are sufficiently acidic to effect such a cleavage, particularly if the rate of alcoholysis in reaction 20 is low. In this connection it should be noted that the alcoholysis of XLI (R is isobutyl) is sufficiently slow so that a 21 per cent yield of the normal ester, ethyl isovalerate, is found among the reaction products

(28). Cleavage of the orthoesters is even more likely with diiminoester salts, such as those derived from malono- and succino-nitriles, in which one of the hydrochloride functions is quite acidic. Indeed the alcoholysis of XLII (reaction 24) gives the mono- and di-orthoesters of succinic acid in approximately equal yields (29); and the diiminomalonic ester dihydrochloride (XLIII) converts ethyl orthophenylacetate to the normal ester (reaction 25) quite readily and completely (5?).

$$ClNH_2{=}(CH_3O)C(CH_2)_2C(OCH_3){=}NH_2Cl \longrightarrow$$
$$XLII$$

$$CH_3OOC(CH_2)_2C(OCH_3)_3 \; + \; (CH_3O)_3C(CH_2)_2C(OCH_3)_3 \quad (24)$$

$$ClNH_2{=}(C_2H_5O)CCH_2C(OC_2H_5){=}NH_2Cl \; + \; C_6H_5CH_2C(OC_2H_5)_3 \longrightarrow$$
$$XLIII$$

$$NH{=}(C_2H_5O)CCH_2C(OC_2H_5){=}NH_2Cl \; +$$
$$C_6H_5CH_2COOC_2H_5 \; + \; C_2H_5Cl \; + \; C_2H_5OH \quad (25)$$
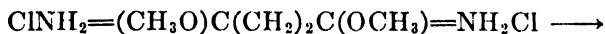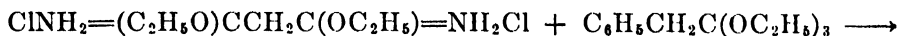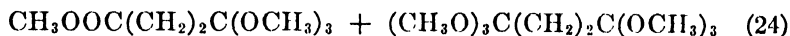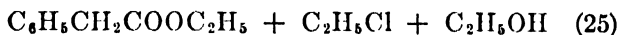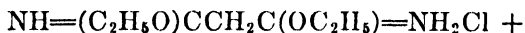
When the ketene acetals are available, they are an excellent source of either simple or mixed orthoesters, as the addition of an alcohol to a ketene acetal (reaction 28) is practically quantitative. This procedure has been used to prepare a wide variety of mixed orthoesters of the type $R_2CHC(OR')_2OR''$ (14, 19, 22).

III. PROPERTIES AND REACTIONS OF KETENE ACETALS

A. PHYSICAL PROPERTIES

The boiling points, refractive indices, and densities of the authenticated ketene acetals that have been reported in the literature, together with the boiling points and refractive indices of the corresponding normal esters and orthoesters in which R'' is a monovalent radical, are listed in table 1. With but one exception (No. 22), the ketene acetal structure is associated with a relatively high boiling point compared to that of the corresponding normal ester. For example, ketene diethylacetal (No. 2) boils 48°C. above the normal ester, ethyl acetate, of which it is the O-ethyl ether, and only 20°C. below the corresponding orthoester, triethyl orthoacetate. Indeed, this ketene acetal boils at about the same temperature as the C-ethyl derivatives of ethyl acetate, ethyl butyrate (b.p. 121°C.), and n-butyl acetate (b.p. 126°C.), each of which contains a highly polarized carbalkoxy group (—COOR). The boiling point of the ketene acetal reflects the high polarization that is associated with this structure. This characteristic is even more strikingly illustrated by the difference between the boiling point of ketene diethylacetal and that of its non-polarized hydrogenation product, acetaldehyde diethylacetal ($CH_3CH(OC_2H_5)_2$). The latter compound, which has approximately the same molecular weight as the ketene acetal, boils 25°C. lower and may be assumed to reflect the contribution of the molecular weight to the boiling point of ketene diethylacetal.

The differences between the boiling points of the ketene dialkylacetals and methylketene diethylacetal (Nos. 2, 3, 4, 5, and 9 of table 1) and the correspond-

TABLE 1

Ketene acetals, RR'C=C(OR")₂, the corresponding esters, RR'CHCOOR" and orthoesters, RR'CHC(OR")₃

NO.	R IS	R' IS	R" IS	KETENE ACETALS			Preparative procedure	Reference	ESTERS		ORTHOESTERS	
				Boiling point	n^{25}_D	d^{25}_4			Boiling point	n^t_D	Boiling point	n^t_D
				°C (mm.)(a)					°C (mm.)(a)		°C (mm.)(a)	
1	H	H	CH₃	89–91	1.3962	0.9274	B	(14)	57	1.3617 (20°)	109	1.3859 (25°)
2	H	H	C₂H₅	124–126	1.4101	0.8876	A, B	(3, 52)	78	1.3805 (25°)	146	1.3941 (25°)
3	H	H	n-C₃H₇	153–154	1.4200	0.879(a)	A	(33)	101	1.3847 (20°)		(i)
4	H	H	i-C₃H₉	180–181	1.4212	0.875(a)	A	(33)	116	1.3901 (20°)		
5	H	H	i-C₄H₁₁	210–211	1.4300	0.856(a)	A	(33)	142	1.4003 (20°)		
6	H	H	C₆H₅	115–116 (1)	1.5583(b)	1.1544	A	(21)	44 (1)	1.503 (20°)	153 (0.5)	
7	H	H	>(CH₂)₂	120–124	1.4465		A	(19)				
8	H	H	>(CH₂)₃	147–155	1.4304		A	(19)				
9	CH₃	H	C₂H₅	133–134	1.4083	0.8654(h)	B	(52)	100	1.3810 (25°)	158	1.4000 (25°)
10	n-C₃H₇	H	CH₃	142–144	1.4235	0.8834	B	(24)	127	1.3993 (15°)	166	1.4090 (24°)
11	n-C₃H₇	H	C₂H₅	167–168	1.4204	0.850	B	(17)	144	1.3989 (25°)	50 (3)	1.4086 (25°)
12	i-C₃H₇	H	C₂H₅	156–157	1.4158	0.8385	B	(17)	134	1.4009 (20°)	59 (7)	1.4056 (25°)
13	n-C₇H₁₅	H	CH₃	100–105 (10)	1.4370(b)	0.8655	B	(24)	95 (10)		140 (45)	1.4255 (21°)
14	C₆H₅	H	CH₃	85–87 (0.5)	1.5390	1.0575	C	(31)	60 (0.5)	1.5050 (20°)	76 (0.4)	1.5065 (20°)
				235–238	1.5620	1.0592	A	(19)	220	1.5091 (16°)		
15	C₆H₅	H	C₂H₅	86–88 (0.2)	1.5385(b)	1.005	C	(31)	69 (0.1)	1.4992 (18°)	91 (0.1)	1.5050 (20°)
				136 (12)			C	(50)	109 (12)			
16	C₆H₅	H	>(CH₂)₂	108–112 (0.8)	1.6075		A	(19)				
17	C₆H₅	H	>(CH₂)₃	124–126 (0.6)	1.5840		A	(19)				
18	CN	H	CH₃	127–128 (11)	1.4630(c)	1.055(c)	C	(30)	92 (11)	1.4177 (25°)	102 (13)	1.4215 (25°)

No.	R₁	R₂	B.p. (mm)	n_D	d	Method	Ref.	B.p. (mm)	n_D	B.p. (mm)	n_D
19	CN	H	145–146 (20)	1.4536 [d]		C	(30)	101 (19)	1.4179 (20°)	118 (19)	1.4189 (25°)
20	$COOC_2H_5$	H	139–140 (17)	1.4609	1.023	C	(46)	96 (18)	1.4162 (20°)	121 (18)	1.4220 (25°)
21	$COOCH_3$	$COOCH_3$	142–145 (13)			D	(1)	130 (16)			
22	C_2H_5O	C_2H_5O	195–196	1.4213	0.949	A	(16)	199	1.4090 (25°)	207	1.4072 (25°)
23	Cl	H	141	1.4460		A	(19)	131	1.4221 (20°)		
24	Cl	H	166	1.4375	1.0534 [b]	A	(35)	145	1.4227 (20°)	182	1.4199 (25°)
25	Cl	Cl	177	1.4350	1.1672 [b]	A	(35)	154	1.4386 (20°)		
26	Br	H	172	1.4880		A	(19)	144	1.4552 (25°)	75 (17)	1.4501 (25°)
27	Br	H	182	1.4610	1.3233 [b]	A	(5)	158	1.4542 (13°)	194	1.4393 (25°)
28	Br	Br	208	1.4895	1.5790 [b]	A	(35)	188	1.5017 (13°)	104 (8)	1.4691 (25°)
29	Cl	$>(CH_2)_2$	89–93 (23)	1.4874		A	(19)				
30	Cl	$>(CH_2)_2$	132–135 (23)	1.4780		A	(19)				
31	Br	$>(CH_2)_2$	118–119 (24)			A	(19)				
32	Br	$>(CH_2)_2$	73–75 (2)	1.5907		A	(19)				
33	Cl	$>(CH_2)_2$	118–121 (21)	[e]		A	(19)				
34	Cl	$>(CH_2)_2$	105–106 (8)	[f]		A	(19)				

(a) Pressures not indicated are atmospheric; the boiling points of esters and orthoesters are generally the upper limits of a 2–3°C. range.

(b) n_D^{20}.

(c) n_D^{40}; d_4^{10}; the melting point of this ketene acetal is 41–42°C.

(d) n_D^{40}; the melting point of this ketene acetal is 37–38°C.

(e) Melting point 55–57°C.

(f) Melting point 67–69°C.

(g) d_{20}^{20}.

(h) d_{35}^{25}.

(i) Melting point 61–62°C.

ing alkyl acetates and ethyl propionate have been offered as evidence that the products obtained by Scheibler and coworkers from these esters in reaction 4 do not have the structures assigned to them (33). In each case the boiling points of the products reported by the German investigators were practically the same as, or even lower than, those of the corresponding esters.

The polarization of the ketene acetals, which is responsible for both their abnormally high boiling points and their extraordinary reactivity, is the result of the unusual hetero-enoid system present in their structures. The *two* alkoxy groups in conjugation with the carbon-to-carbon double bond permit the existence of polarized forms, e.g., Xb, Xc, and Xd, of ketene diethylacetal (X), all of which may be combined in the abbreviated form Xa. Each of these forms contributes to the negative (anionoid or nucleophilic) center on the methylene carbon, which is the seat of the remarkable reactivity of the molecule, and which together with the counterbalancing, though less localized, positive charge produces the permanent polarization that is associated with this structure.
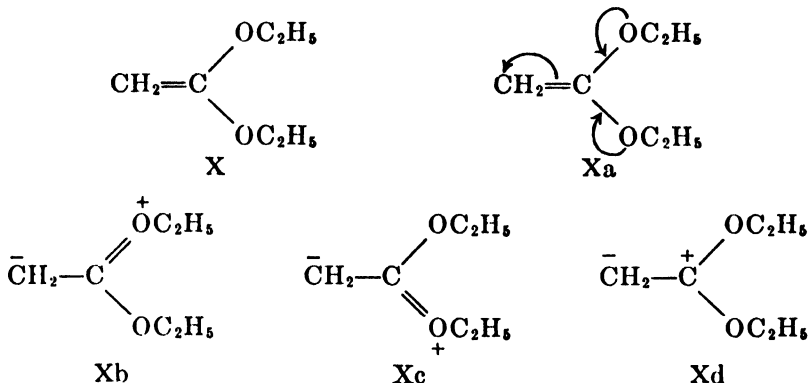
If the methylene group of a ketene acetal carries a substituent, such as phenyl, carbethoxy, or cyano, which through a multiple bond may be involved in further conjugation with the alkoxy groups as in XLIV, the polarization of the molecule is enhanced and the boiling point of the ketene acetal is not only above that of the normal ester, but approaches (No. 15, table 1) or even exceeds (Nos. 14, 18, 19, and 20) that of the orthoester, which has a substantially higher molecular weight.

An interesting relationship of boiling points exists between diethoxyketene diethylacetal (No. 22, table 1) and the corresponding normal ester, ethyl diethoxyacetate. This ketene acetal boils lower than both the ester and the ortho-

ester, doubtless owing to the fact that its polarization is diminished if not eliminated by its symmetrical structure (XLa).
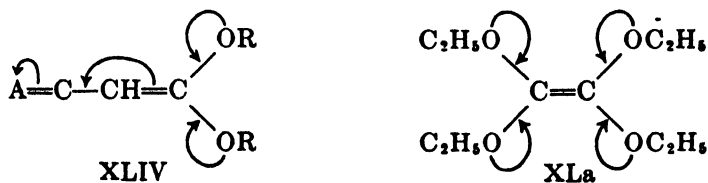
Although there are no esters or orthoesters to which the dioxolanes (Nos. 7, 16, 29, 31, 33) and dioxanes (Nos. 8, 17, 30, 32, 34) of table 1 may be appropriately compared, their boiling points are of interest in relationship to those of the ketene dialkylacetals of comparable molecular weight. For example, 2-methylene-1,3-dioxolane (No. 7) boils considerably above ketene dimethylacetal (No. 1) to which it is comparable in molecular weight; in fact it boils nearly as high as ketene diethylacetal (No. 2), which contains two additional carbons with their complement of hydrogen. A similar relationship exists between the other ketene cyclic acetals and the ketene dialkylacetals that they approximate in molecular weight. Doubtless the higher boiling points of these cyclic acetals are related in part to their cyclic structures *per se*—cyclic compounds generally boil above the related open-chain compounds; *cf.* cyclohexane, b.p. 81°C., and hexane, b.p. 68°C. This structural difference, however, is probably not the sole factor involved; the higher boiling points of the cyclic acetals must be due to a considerable extent to their higher polarizations, because these compounds, as will be seen subsequently, are definitely the most reactive of all the ketene acetals.

The refractive index has proved to be a useful and significant property of the ketene acetals. With the exception of the dichloro- and dibromo-ketene acetals (Nos. 25 and 28), the refractive indices of each of the ketene acetals are substantially higher than either of those of the corresponding ester or orthoester. This value indicates the higher purity of phenylketene dimethylacetal (No. 14) prepared by procedure A than that of the product obtained from procedure C. The refractive indices are useful as a means of distinguishing those ketene acetals (e.g., Nos. 14 and 15) that boil at approximately the same temperatures as the corresponding orthoesters. The change in the refractive index affords a convenient means of following the deterioration of samples of the more reactive ketene acetals.

B. REACTIONS WITH COMPOUNDS CONTAINING ACTIVE HYDROGEN

1. Water

All ketene acetals react with water to form an ester and an alcohol (reaction 26) or in the case of dioxolane or dioxane, an ω-hydroxyalkyl ester (reaction 27).

$$RR'C{=}C(OR'')_2 + HOH \rightarrow [RR'CHC(OR'')_2OH] \rightarrow$$

$$XLV$$

$$RR'CHCOOR'' + R''OH \quad (26)$$

$$RR'C{=}CO(CH_2)_nO + HOH \rightarrow [RR'CHC(OH)O(CH_2)_nO]$$

$$XLVI$$

$$\rightarrow RR'COO(CH_2)_nOH \quad (27)$$
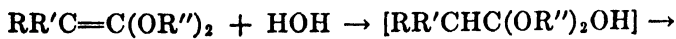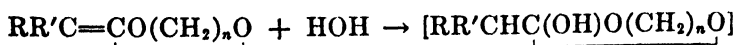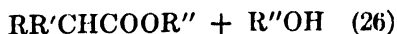
The rates of reactions 26 and 27 vary over a wide range, depending upon the nature of the substituents R, R', and R''. The dimethyl and the cyclic acetals (Nos. 7, 8, 14, 16, 17, 23, 26, 29, 30, 31, and 32 of table 1) have an extraordinary affinity for moisture as shown by a rapid drop in their refractive indices when exposed to the air; for example, phenylketene dimethylacetal is completely converted to a mixture of the corresponding ester and orthoester after exposure to moist air for a few hours (19). The other ketene acetals are more stable in water even to the point where the cyanoketene acetals (Nos. 18 and 19) may be recrystallized from their solutions in hot water (30). However, all of these less reactive ketene acetals react rapidly with water containing a trace of acid.

Whether the orthoacid-esters (XLV and XLVI) are intermediates in the hydrolysis of ketene acetals cannot be determined definitely. The fact that reactions 26 and 27 are strongly catalyzed by hydrogen ions and that other active hydrogen compounds are known to add across the double bonds of ketene acetals make these intermediates appear to be likely possibilities.

2. Alcohols

Primary and secondary alcohols, in the presence of a trace of acid, add rapidly to ketene acetals to yield orthoesters (2, 3, 14) according to reaction 28. In the absence of the acid catalyst the rate of addition varies widely, depending on the substituents on the methylene carbon of the acetal. Tertiary alcohols do not show this reaction and it is for this reason that t-butyl alcohol is the medium generally employed for the dehydrohalogenation of haloacetals in procedure A. In the presence of base the rate of alcohol addition to the haloketene diethylacetals is sufficiently low to permit the isolation of these ketene acetals after the dehydrohalogenation of the dihaloacetaldehyde acetals in ethyl alcohol solution (34).

$$RR'C{=}C(OR'')_2 + R'''OH \xrightarrow{H^+} RR'CHC(OR'')_2OR''' \qquad (28)$$
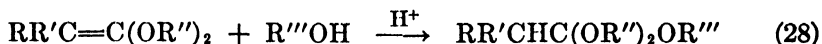
While reaction 28 may be used to prepare mixed alkyl orthoesters (14), it does not yield an alkyl diphenyl orthoester when ketene diphenylacetal is treated with an alcohol; instead, the initially formed mixed orthoester (XLVIII) undergoes alcoholysis to yield phenol (reaction 29), which then reacts with the remaining ketene acetal to form triphenyl orthoacetate (reaction 30), which is the principal product isolated (21).

$$CH_2{=}C(OC_6H_5)_2 + ROH \xrightarrow{H^+} [CH_3C(OC_6H_5)_2OR] \xrightarrow{ROH}$$
$$\text{XLVIII}$$
$$CH_3C(OR)_3 + 2C_6H_5OH \qquad (29)$$

$$CH_2{=}C(OC_6H_5)_2 + C_6H_5OH \rightarrow CH_3C(OC_6H_5)_3 \qquad (30)$$
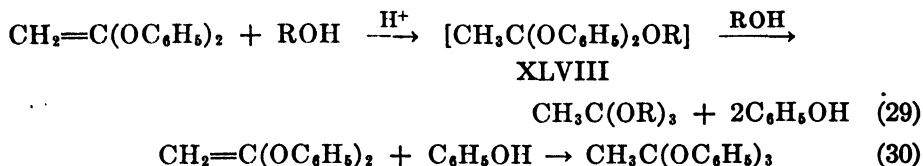
Although phenyl dialkyl orthoacetates undergo pyrolysis to the alkyl acetates and phenetole (reaction 15) when distilled, triphenyl orthoacetate from reaction 30 is quite stable and may be distilled without any evidence of pyrolysis (21).

3. Acids

When ketene diethylacetal is added to an ethereal solution of an acid, it is quantitatively converted to ethyl acetate and the ethyl ester of the acid (or the ethyl ether of a phenol) according to reaction 31. If, however, the order of addition is reversed and the acid added to the ketene acetal there is a secondary reaction, which involves the addition of the acid across two molecules of the ketene acetal (reaction 32) to yield ethyl O-ethylacetoacetate (XLIX).

$$CH_2=C(OC_2H_5)_2 + HX \longrightarrow \left[CH_3C \overset{\diagup OC_2H_5}{\underset{\diagdown X}{-}} OC_2H_5 \right] \longrightarrow$$

$$CH_3COOC_2H_5 + C_2H_5X \quad (31)$$

$$CH_2=C(OC_2H_5)_2 + CH_2=C(OC_2H_5)_2 \longrightarrow$$
$$\text{H---X}$$

$$[CH_3C(OC_2H_5)_2CH_2C(OC_2H_5)X] \rightarrow$$

$$CH_3C(OC_2H_5)=CHCOOC_2H_5 + C_2H_5X + C_2H_5OH \quad (32)$$
$$XLIX$$
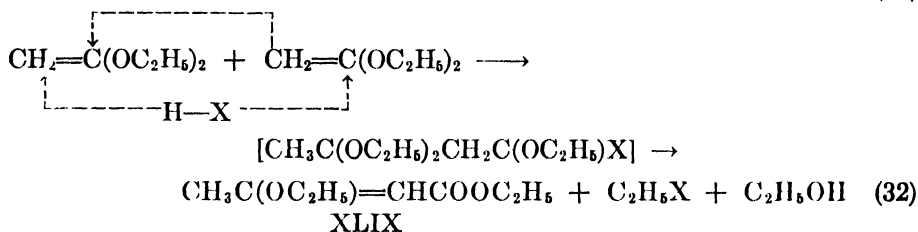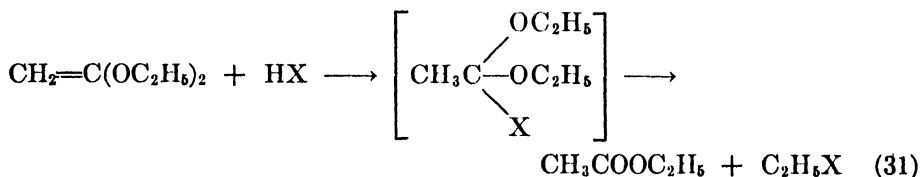
The extent of reaction 32 with a variety of acids is shown in table 2. It is of interest to note that the yield of XLIX is unrelated to the strength of the acid used, the weaker acids giving as high (or higher) yields of this product as the stronger acids. In each of the cases in which a substantial amount of XLIX is formed, an approximately 20 per cent yield of ethyl orthoacetate is also obtained from the addition of the alcohol produced in reaction 32 to a portion of the ketene acetal (reaction 28); the remainder of the acetal follows reaction 31 (26). Hydrogen fluoride occupies a singular position among the acids of table 2; it does not add to the ketene acetal but instead causes it to polymerize (see Section III F).

Ketene diphenylacetal does not follow either reaction 31 or 32 when treated with hydrogen bromide but instead gives polymeric material (21). This is doubtless due to the inability of the strong oxygen–phenyl bond to undergo the rupture required in reaction 31.

With the exception of 2-methylene-1,3-dioxolane, which undergoes a rapid exothermic polymerization when treated with hydrogen chloride, the methylenedioxolanes and methylenedioxanes of table 1 react with this acid to yield ω-chloroethyl and propyl esters in a manner similar to their addition of water in reaction 27 to form hydroxy esters (19).

The addition of one molecule of an acid across two molecules of ketene acetal to form the dimeric product XLIX is reminiscent of 1,4-addition to diolefins. Bromine adds to bromoketene diethylacetal (reaction 57) and maleic anhydride and diazonium salts add to ketene diethylacetal (reactions 47 and 58) in a similar manner.

4. Reactive methylene compounds

The highly enolic dibenzoylmethane reacts with ketene acetal (X) in the same manner as phenols and alcohols to yield the mixed orthoester, L (reaction 33). This reaction is reversible and L reverts to its components—slowly (three months) in a vacuum desiccator or rapidly at 140°C. (2). The reversal of this

TABLE 2

Conversion of ketene diethylacetal to ethyl O-ethylacetoacetate (XLIX) by acids

ACID	YIELD OF XLIX	ACID	YIELD OF XLIX
	per cent		*per cent*
Hydrofluoric...................	0*	Benzoic......................	38
Hydrochloric..................	23	Acetic........................	37
Hydrobromic..................	10	Phenol.......................	0†
Trichloroacetic................	37	p-Bromophenol...............	0†
Chloroacetic..................	42	Tribromophenol..............	26
Formic	35	Trichlorophenol..............	21

* None of either reaction 31 or 32; only polymerization of the ketene acetal.

† Reaction 31 quantitatively.

reaction is analogous to the formation of ketene acetals from orthoesters by procedure C of Section II; also it is of interest to note that this orthoester (L) does not undergo the characteristic decomposition of aryl dialkyl orthoesters shown in reactions 15 and 31.

$$CH_2=C(OC_2H_5)_2 + C_6H_5C(OH)=CHCOC_6H_5 \rightleftarrows$$
$$X$$
$$CH_3C(OC_2H_5)_2OC(C_6H_5)=CHCOC_6H_5 \quad (33)$$
$$L$$
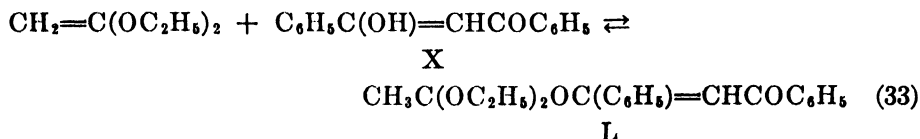
In contrast to the behavior of dibenzoylmethane, the weaker enolic compounds, acetoacetic ester and malonic ester, add to ketene acetal as H— and —CHR₂ to form a carbon-to-carbon linkage (reactions 34 and 35). A remarkable feature of this addition is that it is base-catalyzed. In the absence of base acetoacetic ester gives a 12 per cent yield of LI at 85°C., but malonic ester does not react even at temperatures as high as 200°C. However, in the presence of 1 mole per cent of sodium ethoxide the yield of LI is raised to 55–60 per cent (2) and malonic ester reacts with the ketene acetal at 125°C. to give two products, LIII (in 66 per cent yield) and LIV (in 11 per cent yield), which result from the two modes of alcohol elimination from the intermediate addition product LII in reaction 35 (15). Each of the reaction products, LIII and LIV, may be alkylated to the α-ethoxyvinylmalonic ester, LV (15).

The base-catalyzed reactions 34 and 35 are of particular interest because they are the only ones (which have been observed to date) that do not appear to involve primarily the anionoid methylene carbon of the ketene acetal. Instead, it seems likely that the carbanion of the methylene compound,$:\overset{-}{C}HR_2$, which

$$CH_2=C(OC_2H_5)_2 + H_2CCOOC_2H_5 \xrightarrow{C_2H_5ONa}$$
$$\underset{\underset{COCH_3}{|}}{}$$

$$CH_3\overset{\overset{OC_2H_5}{|}}{C}=CCOOC_2H_5 + C_2H_5OH \quad (34)$$
$$\underset{\underset{COCH_3}{|}}{}$$
LI

$$CH_2=C(OC_2H_5)_2 + H_2C(COOC_2H_5)_2 \xrightarrow{C_2H_5ONa}$$
$$[CH_3C(OC_2H_5)_2CH(COOC_2H_5)_2] \rightarrow$$
LII

$$CH_3C(OC_2H_5)=C(COOC_2H_5)_2 + CH_2=C(OC_2H_5)CH(COOC_2H_5)_2 \quad (35)$$
LIII · LIV

$$\downarrow RX \text{ and } C_2H_5ONa$$

$$CH_2=C(OC_2H_5)CR(COOC_2H_5)_2$$
LV

is formed by the base, attacks the carbonium center of the polarized form Xd (Section IIIA) of the acetal, $\overset{-}{CH_2}\overset{+}{C}(OC_2H_5)_2$, in a manner similar to the reaction of a carbanion with the positive center of a polarized α,β-unsaturated carbonyl compound ($\overset{+}{H_2C}-C=\overset{-}{C}-O$) in the base-catalyzed Michael reaction.

Methylmalonic ester, $CH_3CH(COOC_2H_5)_2$, which has only a single active hydrogen, cannot be caused to react with ketene acetal even in the presence of 1–50 mole per cent of sodium ethoxide and at temperatures up to 200°C. (2). Bis(phenylsulfonyl)methane, $(C_6H_5SO_2)CH_2$, which is sufficiently acidic to dissolve in aqueous alkali, does not add to ketene acetal either alone or in the presence of alkali; instead it produces polymerization of the acetal (2).

5. Amines

The reaction of ammonia and certain amines with ketene acetal strikingly illustrates the anionoid character of the acetal (2). The reactivities of these bases are inversely proportional to their base strength, or proportional to their ability to release a proton (i.e., their acidities) to the methylene group of the ketene acetal. Aniline reacts readily with ketene acetal at 25°C. to give as the main reaction product ethyl N-phenyliminoacetate in 81 per cent yield; a portion of this product reacts further with aniline to form N,N'-diphenylacetamidine (reaction 36). The absence of ethyl orthoacetate from the products of this reaction indicates that the amine reacts sufficiently rapidly to consume all of the ketene acetal before the alcohol which is produced in the reaction can be elim-

inated from the intermediate and react with the ketene acetal to form the orthoester.

Ethylaniline reacts slowly with ketene acetal at 25°C., but quite rapidly at 100°C., to yield N-ethyl-N-(α-ethoxyvinyl)aniline (LVI). An equivalent amount of ethyl orthoacetate also is formed, regardless of the ratio of the original reactants, indicating that this reaction requires the quantities and follows the course shown in reaction 37.

The stronger base ammonia shows no reaction with ketene acetal at 25°C., but when these compounds are heated together for 3 hr. at 100°C., the main reaction products are acetonitrile (55 per cent) and acetamidine (22 per cent). Reaction 38 illustrates the course of this reaction. Piperidine, like ammonia, does not react readily with ketene acetal, but when the latter is heated with a fivefold excess of the refluxing amine for 2 hr., 1,1,1-tripiperidinoethane (LVII) and an equivalent amount of ethyl orthoacetate are produced according to reaction 39.

$$CH_2{=}C(OC_2H_5)_2 + C_6H_5NH_2 \rightarrow [CH_3C(OC_2H_5)_2NHC_6H_5] \rightarrow$$

$$\underset{\displaystyle C_2H_5OH}{\overset{\displaystyle OC_2H_5}{|}} + CH_3\overset{|}{C}{=}NC_6H_5 \xrightarrow{C_6H_5NH_2} CH_3\overset{\displaystyle HNC_6H_5}{\overset{|}{C}}{=}NC_6H_5 + C_2H_5OH \quad (36)$$

$$2CH_2{=}C(OC_2H_5)_2 + C_6H_5NHC_2H_5 \rightarrow$$

$$CH_2{=}C(OC_2H_5)N(C_2H_5)C_6H_5 + CH_3C(OC_2H_5)_3 \quad (37)$$
$$\text{LVI}$$

$$CH_2{=}C(OC_2H_5)_2 + NH_3 \rightarrow \left[CH_3\overset{\displaystyle NH_2}{\overset{|}{C}}(OC_2H_5)_2 \right] \rightarrow$$

$$C_2H_5OH + \left[CH_3\overset{\displaystyle OC_2H_5}{\overset{|}{C}}{=}NH \right] \quad (38)$$

$$C_2H_5OH + CH_3C(NH_2){=}NH \qquad CH_3CN + C_2H_5OH$$

$$2CH_2{=}C(OC_2H_5)_2 + 3HNC_5H_{10} \rightarrow$$

$$CH_3C(NC_5H_{10})_3 + CH_3C(OC_2H_5)_3 + C_2H_5OH \quad (39)$$
$$\text{LVII}$$
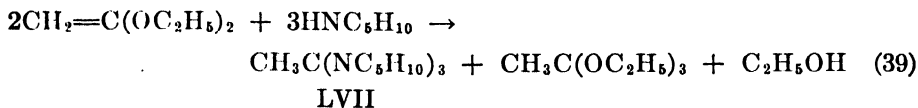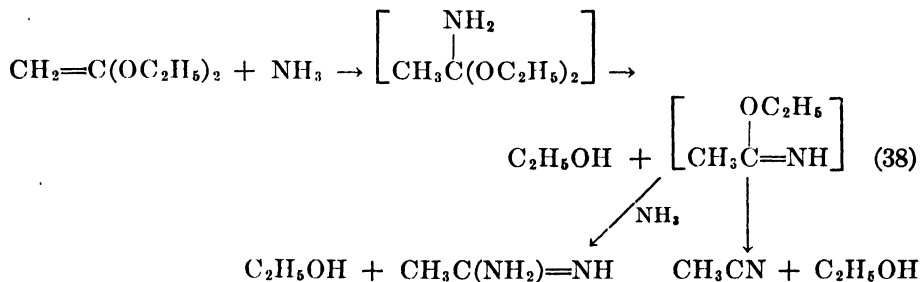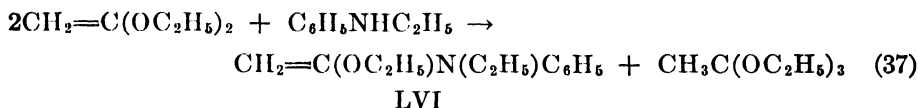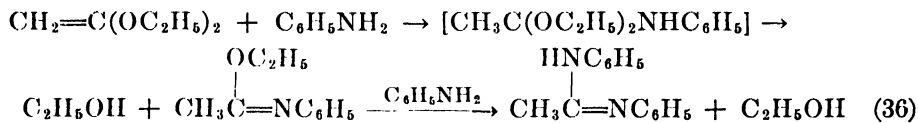
6. Hydrogen

One of the first reactions used to characterize ketene diethylacetal was hydrogenation over Raney nickel (3). Only half of the theoretical quantity of hydrogen was absorbed for complete hydrogenation (reaction 40) because the polymer of the acetal, which formed as the hydrogenation proceeded, deactivated the catalyst. From the products of this hydrogenation a 35 per cent yield of acetaldehyde diethylacetal was separated.

$$CH_2{=}C(OC_2H_5)_2 + H_2 \xrightarrow{Ni} CH_3CH(OC_2H_5)_2 \quad (40)$$
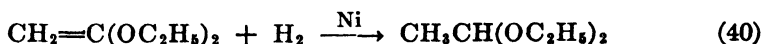
C. ALKYLATION AND ACYLATION OF KETENE ACETALS

1. With alkyl halides

The high anionoid reactivity of ketene acetals indicates that they should undergo a similar type of C-alkylation of the methylene carbon with alkyl halides as do ethyl β-diethylaminocrotonate, $CH_3C(N(C_2H_5)_2)=CHCOOC_2H_5$ (40), and α-methoxystyrene, $C_6H_5C(OCH_3)=CH_2$ (36). Such an alkylation of ketene acetal does indeed occur with n-butyl bromide (reaction 41, R is n-C_4H_9), but the yield of the alkylation product, ethyl caproate, amounts to only 13 per cent of the theoretical because the necessary reaction conditions (72 hr. at 250°C.) are so severe that most of the ketene acetal is pyrolyzed to ethyl acetate and ethylene (reaction 15a). However, with more reactive halides the alkylation occurs under less strenuous conditions and the pyrolysis of the ketene acetal is avoided (26). For example, allyl bromide reacts with the ketene acetal to the extent of 46 per cent at 190°C. for 5 hr., while benzyl bromide reacts in 3 hr. at 125°C. to the extent of 71 per cent.

Both mono- and di-alkylated acetic esters are obtained from these alkylations. It appears that the primary reaction product (LVIII), which results from the addition of the halide across the double bond of the ketene acetal, undergoes pyrolysis in two ways: (a) to eliminate ethyl bromide and yield the monoalkylated acetic ester (LIX) via reaction 41, and (b) to lose hydrogen bromide and yield the monoalkylated ketene acetal (LX), which then is further alkylated via the intermediate LXI to the dialkylacetic ester (LXII) and ethyl bromide (reaction 42).

$$RBr + CH_2=C(OC_2H_5)_2 \rightarrow \left[\begin{array}{c} Br \\ RCH_2C-OC_2H_5 \\ OC_2H_5 \end{array} \right] \rightarrow$$

$$LVIII$$

$$RCH_2COOC_2H_5 + C_2H_5Br \quad (41)$$

$$LIX$$

$$LVIII \rightarrow HBr + RCH=C(OC_2H_5)_2 \xrightarrow{RBr}$$

$$LX$$

$$[R_2CHC(OC_2H_5)_2Br] \rightarrow R_2CHCOOC_2H_5 + C_2H_5Br \quad (42)$$

$$LXI \qquad\qquad LXII$$
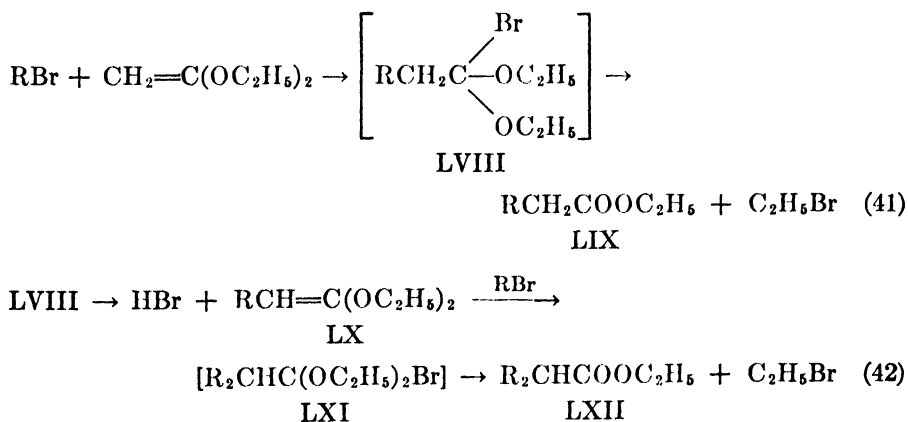
The hydrogen bromide produced in reaction 42 converts an equivalent amount of the ketene acetal to ethyl acetate and ethyl bromide (reaction 31). When allyl bromide is the alkylating agent, the yields of allylacetic ester (LIX: R is allyl) and diallylacetic ester (LXII: R is allyl) are 9 per cent and 31 per cent, respectively; with benzyl bromide the yields of hydrocinnamic ester (LIX: R is benzyl) and dibenzylacetic ester (LXII: R is benzyl) are 14 per cent and 46 per cent, respectively (26).

There is no indication from the study of reactions 41 and 42 that the inter-

mediate LXI undergoes any dehydrohalogenation to yield a dialkylketene acetal in the manner in which the monoalkylated ketene acetal (LX) appears to be formed from LVIII. If such a reaction occurred and the resulting dialkylketene acetal were alkylated, a novel method of preparation of trialkylacetic esters would be available. However, an investigation (24) of the benzylation of mono-alkylated ketene acetals further demonstrates the stability to dehydrohalogena-tion of dialkylated intermediates of the type of LXI. Although the temperature necessary to effect the benzylation of *n*-propylketene diethylacetal causes ex-tensive pyrolysis to ethylene and ethyl valerate (reaction 15a), phenylketene diethylacetal (LX: R is C_6H_5) gives a 59 per cent yield of the monoalkylated product, ethyl α,β-diphenylpropionate, together with a 39 per cent yield of ethyl phenylacetate from the pyrolysis of the ketene acetal. When the more stable *dimethyl* acetals are used, the *n*-propyl-, *n*-heptyl-, and phenyl-ketene acetals yield, respectively, 83 per cent, 87 per cent, and 68 per cent of the mono-benzylated products as in the conversion of LX to LXII in reaction 42; there is no evidence of dibenzylation even with the negative phenyl substituent, which might be expected to activate for dehydrohalogenation the α-hydrogen of such an intermediate as LXI.

Cyanoketene dimethylacetal (LXIII), in contrast to the alkyl- and phenyl-ketene acetals, has in the cyano substituent a group of sufficient negativity to activate for dehydrohalogenation the α-hydrogen of the initial benzylation product (LXIV). Consequently, this ketene acetal undergoes the complete benzylation illustrated in reaction 43 to give the following yields of reaction products: 21 per cent of methyl benzylcyanoacetate (LXV), 26 per cent of methyl dibenzylcyanoacetate (LXVI), and 31 per cent of methyl cyanoacetate (30); the latter product results from the reaction of the ketene acetal (LXIII) with the hydrogen bromide eliminated from the intermediate (LXIV).

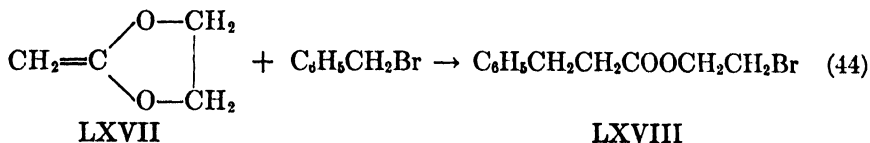$$\text{CNCH}{=}\text{C(OCH}_3)_2 + \text{C}_6\text{H}_5\text{CH}_2\text{Br} \rightarrow \begin{bmatrix} \overset{\displaystyle \text{CN}}{\underset{\displaystyle}{|}} \;\; \overset{\displaystyle \text{OCH}_3}{\nearrow} \\ \text{C}_6\text{H}_5\text{CH}_2\text{CHC}{-}\text{OCH}_3 \\ \underset{\displaystyle \text{Br}}{\searrow} \end{bmatrix}$$

LXIII   LXIV

$$\text{C}_6\text{H}_5\text{CH}_2\overset{\displaystyle \text{CN}}{\underset{\displaystyle |}{\text{C}}}{=}\text{C(OCH}_3)_2 \qquad \text{C}_6\text{H}_5\text{CH}_2\text{CH(CN)COOCH}_3$$

−HBr   −CH$_3$Br

LXV

$$\downarrow \text{C}_6\text{H}_5\text{CH}_2\text{Br}$$

$$[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C(CN)C(OCH}_3)_2\text{Br}] \xrightarrow{-\text{CH}_3\text{Br}} (\text{C}_6\text{H}_5\text{CH}_2)_2\text{C(CN)COOCH}_3 \qquad (43)$$
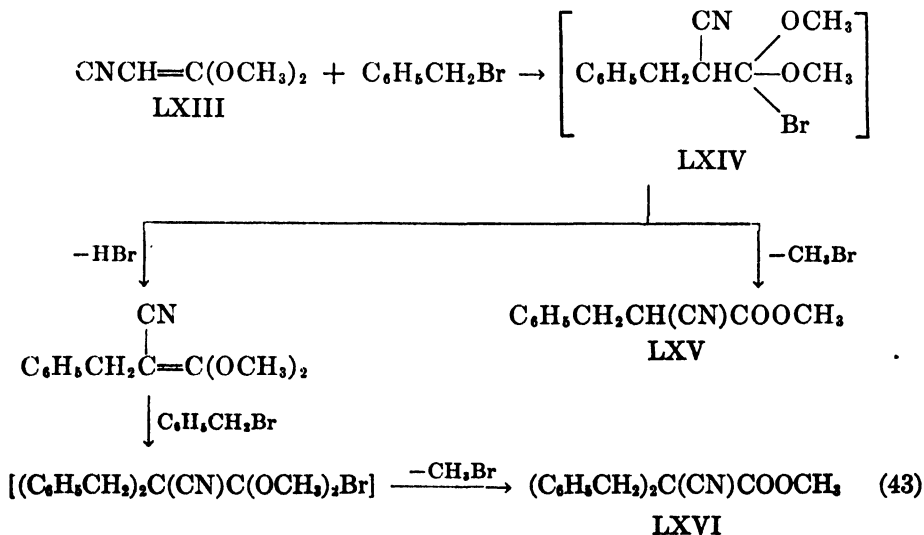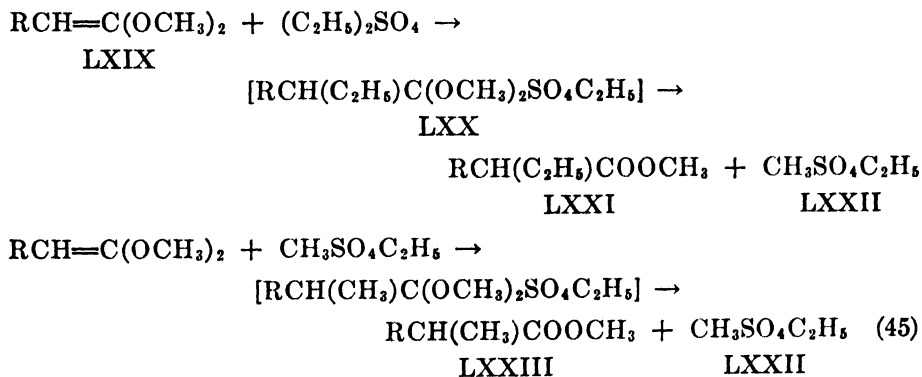
LXVI

In contrast to the extensive dialkylation of ketene diethylacetal in reactions 41 and 42, 2-methylene-1,3-dioxolane (LXVII) reacts with benzyl bromide at 150°C. to yield only the monoalkylation product, β-bromoethyl hydrocinnamate (LXVIII), as shown in reaction 44. The yield amounts to only 43 per cent because of the rapid concurrent polymerization of this cyclic ketene acetal (19).

$$CH_2=C\overset{O-CH_2}{\underset{O-CH_2}{\Big\langle}} \quad + \quad C_6H_5CH_2Br \rightarrow C_6H_5CH_2CH_2COOCH_2CH_2Br \quad (44)$$

$$\text{LXVII} \qquad\qquad\qquad\qquad \text{LXVIII}$$

2. With alkyl sulfates

The alkylation of n-propylketene dimethylacetal (LXIX: R is n-propyl) with diethyl sulfate at 145°C. for 15 hr. gives, surprisingly, a 65 per cent yield of methyl α-*methyl*valerate (LXXIII) together with a 20 per cent recovery of the unchanged ketene acetal (24). This unexpected alkylation behavior is explained by the sequence of transformations shown in reaction 45. The conversion of the ketene acetal (LXIX) to LXXIII instead of LXXI is due to the greater reactivity of methyl ethyl sulfate (LXXII), which is eliminated from the intermediate LXX, as a methylating agent than as an ethylating agent. The rate of methylation appears to be sufficiently high to exclude an appreciable amount of ethylation after some of the mixed sulfate (LXXII) is formed, as none of the α-ethylated ester (LXXI) is found among the reaction products even though a large excess of diethyl sulfate is present in the reaction mixture.

$$RCH=C(OCH_3)_2 + (C_2H_5)_2SO_4 \rightarrow$$
$$\text{LXIX}$$
$$[RCH(C_2H_5)C(OCH_3)_2SO_4C_2H_5] \rightarrow$$
$$\text{LXX}$$
$$RCH(C_2H_5)COOCH_3 + CH_3SO_4C_2H_5$$
$$\text{LXXI} \qquad\qquad \text{LXXII}$$

$$RCH=C(OCH_3)_2 + CH_3SO_4C_2H_5 \rightarrow$$
$$[RCH(CH_3)C(OCH_3)_2SO_4C_2H_5] \rightarrow$$
$$RCH(CH_3)COOCH_3 + CH_3SO_4C_2H_5 \quad (45)$$
$$\text{LXXIII} \qquad\qquad \text{LXXII}$$

R is n-C₃H₇.

The continual regeneration of the methylating agent (LXXII) in reaction 45 indicates that the alkyl sulfate merely serves as a carrier of one of the methyl groups from the oxygen to the methylene carbon of the ketene acetal. Consequently, it would be expected that catalytic amounts of dimethyl sulfate would serve to convert the acetal (LXIX) to the α-methylated ester (LXXIII). This is indeed the case; when one equivalent of the ketene acetal is heated with 0.05 equivalent of dimethyl sulfate, 0.3 equivalent of LXXIII is produced (24).

3. With acyl halides

Ketene diethylacetal (X) reacts exothermically with *one* equivalent of acetyl chloride at room temperature to give a 30 per cent yield of O-acetylacetoacetic ester (LXXIV), as shown in reaction 16. The hydrogen chloride produced in this reaction converts a portion of the ketene acetal to O-ethylacetoacetic ester (XLIX) (reaction 32). When the molar ratio of acetyl chloride to the ketene acetal is increased to 3:1, the yield of LXXIV is increased to 52 per cent. Aceto-acetic ester is shown to be an intermediate in reaction 46 by (a) the separation of a small amount (3 per cent) from the reaction products and (b) the acetylation of acetoacetic ester with acetyl chloride (the final step of reaction 46) in the presence of ketene acetal, which absorbs the hydrogen chloride, to a mixture of the isomeric O- and C-acetal derivatives in 79 per cent yield (26). The C-acetyl derivative is formed by the rearrangement of LXXIV.

$$CH_2\!\!=\!\!C(OC_2H_5)_2 \;+\; CH_3COCl \;\rightarrow$$
$$X$$

$$C_2H_5Cl \;+\; CH_3COCH_2COOC_2H_5 \xrightarrow{\;CH_3COCl\;}$$

$$\overset{\displaystyle OCOCH_3}{\underset{\displaystyle LXXIV}{CH_3\overset{|}{C}\!\!=\!\!CHCOOC_2H_5}} \;+\; HCl$$

$$HCl \;+\; X \xrightarrow{\;via\ \text{reaction 32}\;} \overset{\displaystyle OC_2H_5}{\underset{\displaystyle XLIX}{CH_3\overset{|}{C}\!\!=\!\!CHCOOC_2H_5}} \qquad (46)$$
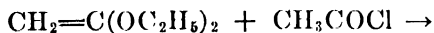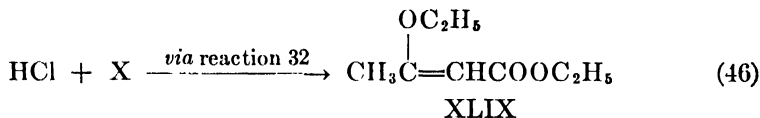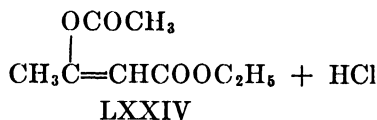
Benzoyl chloride does not react as readily with ketene acetal (X) as does acetyl chloride, but after 2 hr. at 100°C. a 59 per cent yield of ethyl O-benzoyl-benzoylacetate, $C_6H_5C(OCOC_6H_5)\!\!=\!\!CHCOOC_2H_5$, which corresponds to LXXIV of reaction 46, is obtained (26). Similarly, n-propylketene dimethylacetal (LXIX: R is n-C_3H_7) reacts with benzoyl chloride to give a 60 per cent yield of methyl O-benzoyl-α-benzoylvalerate, $C_6H_5C(OCOC_6H_5)\!\!=\!\!C(CH_2CH_2CH_3)COOCH_3$ (24). In contrast to ketene and n-propylketene acetals, chloroketene diethylacetal fails to show any significant amount of reaction with benzoyl chloride (24).

Benzenesulfonyl chloride does not acylate ketene acetal, but instead causes it to polymerize. A considerable portion of the sulfonyl chloride is recovered un-changed after being heated with the acetal for 2 hr. at 125°C. The remainder of the sulfonyl chloride is recovered as ethyl benzenesulfonate, which is formed from the alcohol eliminated from the polymer; the use of a higher ratio of the ketene acetal to the sulfonyl chloride only serves to increase the yield of this ester (26). It seems likely that there is some significance, as yet undeter-mined, to the fact that such structurally different sulfur compounds as ben-zenesulfonyl chloride and bis(phenylsulfonyl)methane (Section III B) produce a polymerization of ketene diethylacetal rather than react in the manner of their carbon analogs.

D. REACTIONS WITH α,β-UNSATURATED CARBONYL COMPOUNDS

1. Maleic anhydride

This dienophile in ether solution readily adds across two molecules of ketene diethylacetal in the 1,4 manner, previously noted with acids in reaction 32, to give 3,5-diethoxy-1,6-dihydrophthalic anhydride (LXXVI) in 70 per cent yield, as shown in reaction 47. The intermediate LXXV is doubtless the precursor of LXXVI, and the alcohol lost from this intermediate converts two equivalents of the ketene acetal to ethyl orthoacetate. Consequently a 4:1 ratio of the ketene acetal to the maleic anhydride is required for the maximum yield of LXXVI, which precipitates quite completely from the ether solution. However, with benzene as the solvent for these reactants, LXXVI is not formed but instead the anhydride of the tetracarboxylic acid, LXXVII. As this latter compound also is formed quite readily when LXXVI is allowed to react with maleic anhydride in benzene solution, the formation of LXXVI exclusively in ether solution appears to be due to its insolubility in this solvent and its consequent precipitation as rapidly as it is formed and before it can react further with the maleic anhydride to produce LXXVII (18).

The anhydride LXXVI is characterized by its hydrolysis via the intermediate LXXVIII to the ketodibasic acid LXXIX, which is readily decarboxylated to the monobasic acid LXXX. Dehydrogenation of LXXVI by palladium yields 3,5-diethoxyphthalic anhydride LXXXI, the acid (LXXXII) of which also may be obtained from the reaction of ketene acetal with diethyl acetylene-dicarboxylate as shown in reaction 48 (18).

Although maleic anhydride condenses with ketene acetal as shown in reaction 47 at room temperature, dimethylmaleic anhydride does not react with the acetal even after 12 hr. in refluxing benzene. At 175–180°C. a reaction does occur, as none of the original reactants are recovered, but it has not been possible to isolate any definite product from the reaction mixture (18).

2. α,β-Unsaturated ketones

Benzalacetophenone (LXXXIII: R is C_6H_5) and dibenzalacetone (LXXXIII: R is $HC{=}CHC_6H_5$) when heated at 125°C. with an excess of ketene acetal add to only one equivalent of the acetal (reaction 49) to yield the cyclobutane derivatives (LXXXIV), which are characterized by hydrolysis to the corresponding β-phenyl-γ-acylbutyric acids (LXXXV). The yields of the cyclobutane derivatives (LXXXIV) are 87–91 per cent. There is no elimination of alcohol from either of these products, as shown by their analyses and the absence of ethyl orthoacetate in the reaction mixture (18).

$$C_6H_5CH{=}CHCOR + CH_2{=}C(OC_2H_5)_2 \rightarrow$$

LXXXIII

$$\underset{\text{LXXXIV}}{\begin{array}{c} C_6H_5CH{-}CHCOR \\ | \quad\quad | \\ CH_2{-}C(OC_2H_5)_2 \end{array}} \xrightarrow{H_2O} \underset{\text{LXXXV}}{\begin{array}{c} C_6H_5CHCH_2COR \\ | \\ CH_2COOH \end{array}} \quad (49)$$

A complex chemical reaction scheme (rotated). Key structures and labels:

$(C_2H_5O)_2C$ — CH_2

$CH_2=C(OC_2H_5)_2$

$+$

$CH-CO$, O, $CH-CO$ (maleic anhydride)

ether solution

benzene solution

maleic anhydride in benzene solution

LXXV

$(C_2H_5O)_2C$ CH_2 $CH-CO$ O $CH-CO$ $CH-C(OC_2H_5)_2$ H_2C C

$+ 2C_2H_5OH$

$CH_2=C(OC_2H_5)_2 \longrightarrow CH_3C(OC_2H_5)_3$

LXXVI

C_2H_5O CH_2 $CH-CO$ O CO $C=$ HC $C-OC_2H_5$

H_2O

Pd

LXXXI

C_2H_5O CO O CO OC_2H_5

$\xrightarrow{H_2O}$

LXXXII

C_2H_5O $COOH$ $COOH$ OC_2H_5 (48)

$^{(47)}$

LXVIII

C_2H_5OC CH_2 $CHCOOH$ $CCOOH$ C HC OC_2H_5

C_2H_5O $COOC_2H_5$ $COOC_2H_5$ OC_2H_5

LXXIX

C_2H_5OC CH_2 $CHCOOH$ $CHCOOH$ C HC O

$-CO_2$ $85°C.$

LXXX

C_2H_5OC CH_2 $CHCOOH$ CH_2 C HC O

$+$ $2CH_2=C(OC_2H_5)_2$

$CCOOC_2H_5$ $CCOOC_2H_5$

LXXVII

C_2H_5OC OC_2H_5 CH_2 C $HCCO$ O $HCCO$ CH C C O O HC O

480

With benzalacetone (LXXXIII: R is CH_3) in reaction 49 ethyl acetate and ethyl orthoacetate are the only reaction products isolated; the major portion of the reaction mixture is a non-distillable tar, which indicates the formation of self-condensation products from the benzalacetone and polymerization of the ketene acetal. Phorone, $(CH_3)_2C=CHCOCH=CH(CH_3)_2$, does not react with ketene acetal even after 12 hr. at 125°C.; in this case practically all of the ketene acetal is recovered unchanged. The inertness of this di-α,β-unsaturated ketone is attributed to the deactivating influence of the *gem*-dimethyl substituents (18).
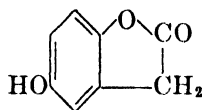
3. Quinones

The reaction between benzoquinone and ketene diethylacetal starts at about 80°C. and, without a solvent, becomes so violent that it cannot be controlled; in benzene solution, however, the reaction proceeds smoothly. The product of this reaction, which involves the condensation of one molecule of the quinone with one of the acetal followed by the loss of alcohol, is isolated in 61 per cent yield. Originally it was thought to be the bicyclooctadiene LXXXVI (18), but later work with other quinones (20) shows it to have the ethoxycoumarone structure (LXXXVII). Hydrogen bromide converts LXXXVII to 5-hydroxy-2-coumaranone (LXXXVIII) and hydrolysis converts it to hydroquinoneacetic (homogentisic) acid (LXXXIX).
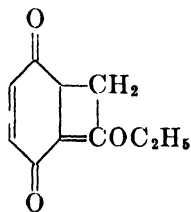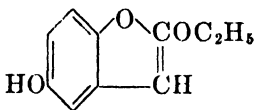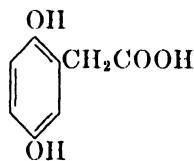

LXXXVI   LXXXVII   LXXXVIII   LXXXIX

m-Xyloquinone, bromobenzoquinone, 2,5-dibromobenzoquinone, and 1,4-naphthoquinone react with ketene acetal in a manner similar to benzoquinone to give coumarones corresponding to LXXXVII. These reactions appear to involve a 1,4-addition of the acetal as H and $CH=C(OC_2H_5)_2$ to the quinone, followed by the enolization and lactonization of the resulting intermediate, as the formation of LXXXVII is illustrated in reaction 50. *p*-Xyloquinone and 2,6-dibromobenzoquinone react with the ketene acetal, but it has not been possible to isolate any definite condensation product from the tarry products resulting from either of these reactions. Duroquinone does not react with the ketene acetal and is recovered unchanged after a reaction period of 12 hr. at 150°C. (20).

In contrast to the bromobenzoquinones, bromo-1,4-naphthoquinones react with ketene acetal to eliminate ethyl bromide and attach the quinone residue to the methylene carbon in the manner of the alkylation and acylation reactions of Section III C. With 2-bromo-1,4-naphthoquinone the reaction continues with a second molecule of the ketene acetal to give xanthopurpurin diethyl ether (XC)

in 21 per cent yield (reaction 51). The hydrogen bromide which is postulated as an elimination product of the first intermediate does not appear as such but as ethyl bromide (obtained in 40 per cent yield) from the reaction of the acid with ketene acetal. The formation of XC with the evolution of ethyl bromide also may be rationalized by assuming the addition of the bromoquinone across two molecules of the ketene acetal in the 1,4 manner of reaction 32 instead of the

$$\rightarrow \text{LXXXVII} \quad (50)$$

$$\text{HBr} +$$

$$2C_2H_5OH +$$

$$\text{XC} \quad (51)$$

$$\xrightarrow{CH_2=C(OC_2H_5)_2} C_2H_5Br +$$

$$\text{XCI} \quad (52)$$
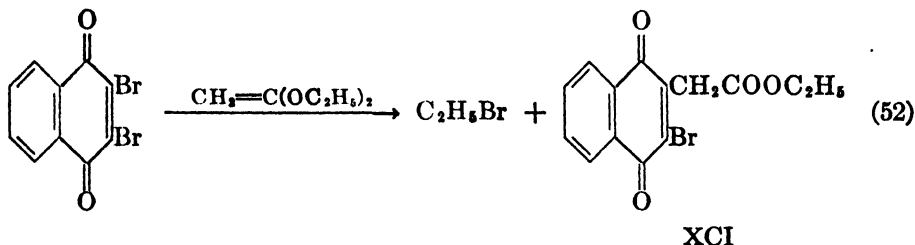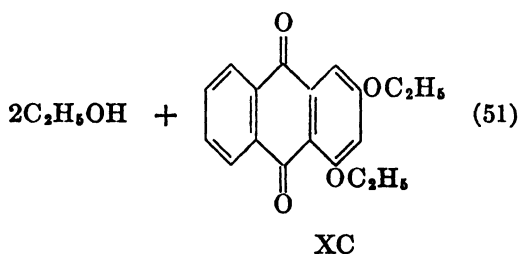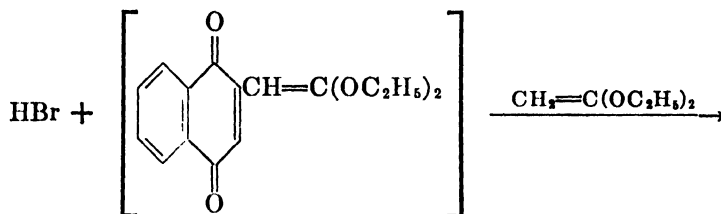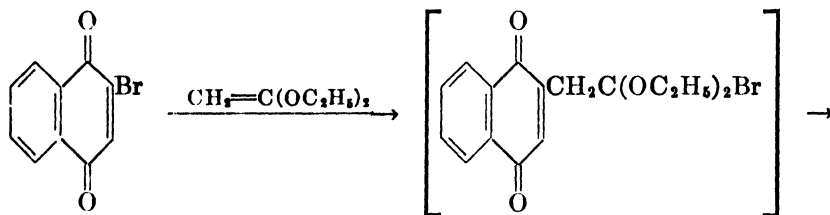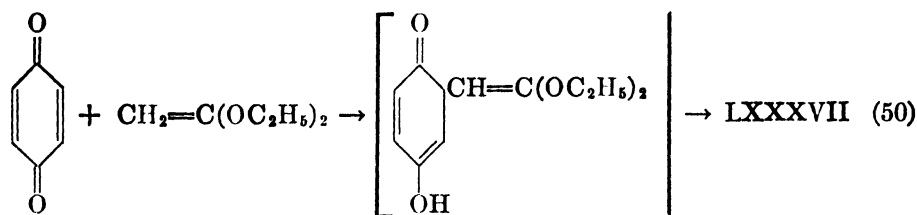
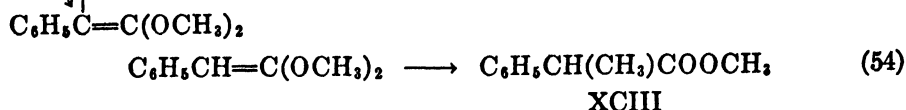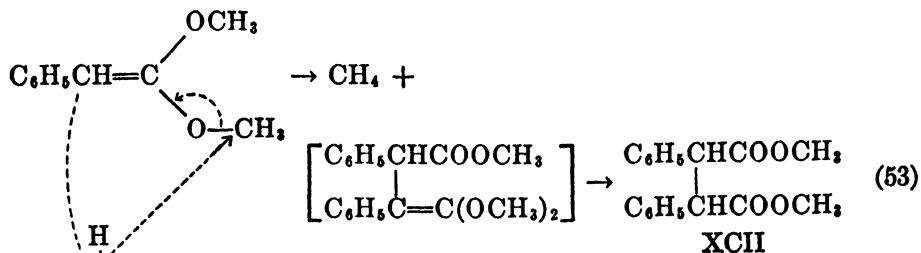two-step process shown in reaction 51. However, none of the alkylations or acylations of Section III C show any of this type of addition, and for this reason it is believed that reaction 51 initially follows the pattern of reaction 42. With 2,3-dibromo-1,4-naphthoquinone only one equivalent of the ketene acetal appears in the reaction product, ethyl 3-bromo-1,4-naphthoquinon-2-ylacetate (XCI), which is produced in 58 per cent yield according to reaction 52 (20).

The addition of ketene acetal to quinones is greatly influenced by the substituents on the quinone nucleus. While benzoquinone gives a 61 per cent yield of LXXXVII in reaction 50, the more drastic conditions required to produce a reaction with the xyloquinones permit the isolation of only 7 per cent of the coumarone corresponding to LXXXVII in the case of m-xyloquinone; the remainder of the reaction mixture is a tar, as is the entire product from the reaction with p-xyloquinone. This behavior indicates extensive polymerization of the intermediate products of the type shown in reaction 50. Even though 1,4-naphthoquinone reacts more readily with ketene acetal than do the xyloquinones, tar formation is extensive in this case also and the pure benzocoumarone is obtained in low (2 per cent) yield. Bromo substituents in the benzoquinone nucleus activate it for reaction with the ketene acetal and distinctly higher yields (27–40 per cent) of the coumarones or their degradation products are obtained from the bromobenzoquinones. In reactions 51 and 52 the bromonaphthoquinones behave as acyl halides (cf. reaction 46), of which they are indeed vinylogs, and add to the double bond of the ketene acetal.

E. PYROLYSIS

The pyrolysis of various ketene diethylacetals to ethylene and the normal esters (see reactions 12 and 15a) has been discussed above in connection with the pyrolysis of orthoesters (Section II C). Also, mention has been made of the facile rearrangement of ketene diallyl- and dibenzyl-acetals to the corresponding allyl- and benzyl-acetic esters when an attempt is made to prepare these ketene acetals from the bromoacetals by reaction 7.

Under conditions (6 hr. at 200°C.) that cause the complete pyrolysis of ketene

$$C_6H_5CH=C\begin{matrix}OCH_3\\O-CH_3\end{matrix} \rightarrow CH_4 +$$

$$\begin{bmatrix}C_6H_5CHCOOCH_3\\C_6H_5C=C(OCH_3)_2\end{bmatrix} \rightarrow \begin{matrix}C_6H_5CHCOOCH_3\\C_6H_5CHCOOCH_3\end{matrix} \quad (53)$$

$$\text{XCII}$$

$$C_6H_5C=C(OCH_3)_2$$

$$C_6H_5CH=C(OCH_3)_2 \longrightarrow C_6H_5CH(CH_3)COOCH_3 \quad (54)$$

$$\text{XCIII}$$

diethylacetal (shown in reaction 15a), ketene dimethylacetal is unaffected. In fact, 95 per cent of the dimethylacetal is recovered after heating at 200°C. for 24 hr. (14).

When phenylketene dimethylacetal is heated at 250–260°C. methane is evolved and meso-α,α'-diphenylsuccinate (XCII) is formed in 21–29 per cent yields. This pyrolysis appears to involve the elimination of a hydride ion from one molecule of the ketene acetal with a methyl cation from another molecule, as shown in reaction 53. In addition to the succinic ester (XCII) a 22 per cent yield of methyl α-phenylpropionate (XCIII) is produced by the rearrangement of the ketene acetal (reaction 54) (31).

A small amount of the ethyl ester corresponding to XCII is formed during the pyrolysis of ethyl orthophenylacetate to phenylketene diethylacetal (reaction 3). It seems likely that the ketene acetal is the precursor of this product as it is of XCII in reaction 53 (31).
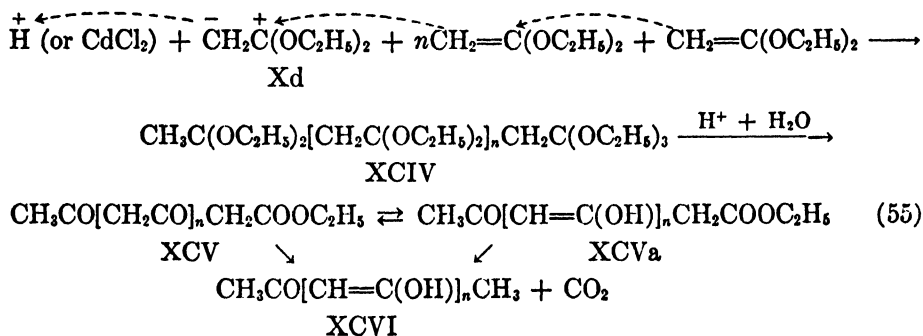
F. POLYMERIZATION

One of the first chemical properties of ketene diethylacetal to be noticed was its tendency to polymerize (3). The polymer appeared as a thin white deposit on the interior of flasks and condensers in which the compound had been distilled and also as a semisolid gum that separated from distilled samples after standing a few days. The cause of this type of polymerization was traced to the acidic glass surfaces of the apparatus; it was generally excessive in apparatus that had been cleaned with ordinary chromic acid–sulfuric acid mixture, and it could be practically eliminated by treatment of such acid-washed apparatus with aqueous alkali solution, followed by rinsing and drying. Similarly, dusting the interior of alkali-washed containers with potassium or sodium t-butoxide prevented polymerization of the acetal during storage (12).

The polymerization of ketene acetal by acidified glass surfaces is, presumably, the result of the coördination of a proton with the anionoid methylene group of the acetal, which is shown in reaction 55 as the polarized form Xd (see Section III A), to produce a highly reactive carbonium ion. Since there is no anion available from the glass surface to add to this carbonium ion, as there is with the simpler acids employed in reactions 31 and 32, a chain reaction is initiated and propagated by the successive coördination of the anionoid centers of other ketene acetal molecules with this and similar subsequently formed positive centers (reaction 55).

Other compounds capable of coördinating with the anionoid center of the ketene acetal are more efficient catalysts for this polymerization than are acidified glass surfaces (12). A wide variety of metal chlorides and such non-ionic acids as boron fluoride and aluminum chloride are powerful catalysts for the polymerization. Benzoyl peroxide, which catalyzes the polymerization of many vinyl compounds, has no appreciable effect on ketene acetal, indicating that the polymerization of the acetal does not follow a free-radical mechanism but rather the ionic course shown in reaction 55.

The most satisfactory polymer is obtained with cadmium chloride as the

catalyst. This polymer, which is a white powder with approximately the same carbon, hydrogen, and ethoxyl content as the monomer, has the "head-to-tail" structure (XCIV). It is remarkably stable to alkali and heat, but is quite sensitive to acids. It gradually changes to a brownish-red powder on exposure to the laboratory air for 24 hr.; dilute acids at room temperature convert it immediately to a water-insoluble, red oil; refluxing dilute acid converts it to a reddish-black oil which solidifies to a brittle glass on cooling. Both of these red polymers are soluble in aqueous sodium hydroxide solution but are quite insoluble in other solvents; the difference between them appears to be in the extent to which the ethoxyl groups have been removed by hydrolysis. The color and alkali-solubility of this red hydrolysis product indicate it to be a poly-1,3-diketone (XCV), which in the enolic form (XCVa) is highly conjugated.

$$H \text{ (or } CdCl_2) + CH_2C(OC_2H_5)_2 + nCH_2{=}C(OC_2H_5)_2 + CH_2{=}C(OC_2H_5)_2 \longrightarrow$$
$$Xd$$

$$CH_3C(OC_2H_5)_2[CH_2C(OC_2H_5)_2]_nCH_2C(OC_2H_5)_3 \xrightarrow{H^+ + H_2O}$$
$$XCIV$$

$$CH_3CO[CH_2CO]_nCH_2COOC_2H_5 \rightleftarrows CH_3CO[CH{=}C(OH)]_nCH_2COOC_2H_5 \quad (55)$$
$$XCV \qquad\qquad\qquad XCVa$$
$$CH_3CO[CH{=}C(OH)]_nCH_3 + CO_2$$
$$XCVI$$

The amount of carbon dioxide evolved during the hydrolysis of XCIV to XCVI indicates the molecular weight of the polymer (XCIV) to be 2600–2700, i.e., n is 20–21. This value for the molecular weight is indicated also by the amount of acetic acid produced by the vigorous oxidation of the polyketoester (XCV). Both of these methods of molecular weight determination, however, serve only to measure the average length of the unit chains (XCIV), which may undergo cross-linking through inter-unit loss of alcohol. The insolubility of the polymer in organic solvents indicates that some of this cross-linking has occurred, but it is not extensive as the ethoxyl content of the polymer is very little lower than that of ketene acetal (12).

Along with the polymer XCIV, small amounts of the dimer (XCVII), of the open-chain trimer (XCVIII), and of 1,3,5-triethoxybenzene (C), the last of which results from the loss of alcohol from the cyclic trimer (XCIX), are formed in the cadmium chloride-catalyzed polymerization of ketene acetal (12).

As previously noted in table 2 of Section III B, hydrogen fluoride causes polymerization of ketene diethylacetal. Depending on the concentration of the acetal in an ether solution, various types of polymers may be obtained with catalytic amounts of hydrogen fluoride (27). This catalyst is particularly useful for the production of the trimers, XCVIII and XCIX. For example, a 1 per cent solution of ketene diethylacetal in ether is converted by 5 mole per cent of hydrogen fluoride to the dimer and the trimers in 12–14 per cent and 40–45 per
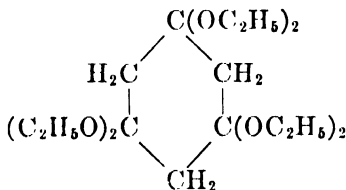
cent yields, respectively. From the latter fraction the cyclic trimer, 1,1,3,3,5,5-hexaethoxycyclohexane (XCIX), m.p. 72–74°C., may be isolated in yields amounting to 22 per cent of the weight of the polymerized ketene acetal. This cyclic trimer is characterized by its ready conversion to C (in 85 per cent yield) and by its hydrolysis to phloroglucinol with carbonic acid (27).

$$CH_3C(OC_2H_5)_2CH=C(OC_2H_5)_2 \qquad CH_3C(OC_2H_5)_2CH_2C(OC_2H_5)_2CH=C(OC_2H_5)_2$$

<div align="center">

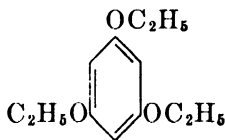XCVII   XCVIII

</div>

<div align="center">

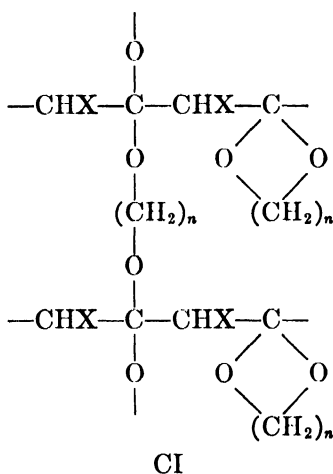XCIX   C

</div>

In contrast to the unsubstituted ketene acetal shown in reaction 55, the halogenated ketene diethylacetals (12) and methylketene diethylacetal (27) do not polymerize. For example, chloroketene diethylacetal is recovered unchanged after heating with cadmium chloride at 110°C. for 70 hr.; and methylketene diethylacetal reacts with hydrogen fluoride, as it does with other acids, to give ethyl propionate and ethyl fluoride.

The 2-methylene-1,3-dioxolanes and -1,3-dioxanes, the ketene cyclic acetals of table 1, in contrast to the diethylacetals, are characterized by their marked tendency to undergo *spontaneous* polymerization. Only those having a phenyl or two chlorine substituents on the methylene carbon (Nos. 16, 17, 33, and 34) are relatively resistant to polymerization. The other cyclic acetals (Nos. 7, 8, 29, 30, 31, and 32) are obtained pure only with the greatest difficulty because of the polymerization that occurs during their isolation. The use of alkali-washed glassware lowers the rate but does not prevent this polymerization; varying amounts of a voluminous white precipitate generally are present in all freshly distilled samples. The rate of polymerization appears to be related to the purity of the ketene cyclic acetal, i.e., the more pure the acetal the more rapidly it polymerizes. When the polymerization is slight, the ketene acetal usually is found to be contaminated with the ester resulting from the reaction of water with the acetal (reaction 27) (19).

Two types of polymers result from the spontaneous polymerizations of these cyclic acetals. Those from the unsubstituted methylenedioxolane and methylenedioxane (Nos. 7 and 8 of table 1) are solids, which melt over a relatively narrow range and which are hydrolyzed by dilute hydrochloric acid to red, alkali-soluble oils similar to those obtained from the cadmium chloride-polymerized ketene diethylacetal in reaction 55. The polymers obtained from the mono-halogenated acetals (Nos. 29–32 of table 1) are talc-like powders that do not melt, but sinter in the range of 290–350°C. They are insoluble in all solvents except

concentrated sulfuric acid (from which they cannot be recovered by dilution with water) and remain unaffected after heating for several hours with concentrated hydrochloric acid (19).

Both types of these polymers give the same analytical data as the values calculated for the monomers. Their properties lead to the conclusion that the polymers formed from the methylenedioxolane and methylenedioxane (Nos. 7 and 8) are relatively simple straight chains of the type of XCIV of reaction 55 with a minimum of cross-linking. The more refractory character of the polymers of the monohalogenated ketene cyclic acetals suggests that the chains of these polymers are extensively cross-linked through the bifunctional glycol moieties to form the more complex structure illustrated in part in formula CI (19).

$$
\begin{array}{c}
\mid \\
\mathrm{O} \\
\mid \\
-\mathrm{CHX-C-CHX-C-} \\
\mid \qquad\qquad /\ \backslash \\
\mathrm{O} \qquad \mathrm{O} \quad \mathrm{O} \\
\mid \qquad\quad \backslash\ / \\
(\mathrm{CH_2})_n \quad (\mathrm{CH_2})_n \\
\mid \\
\mathrm{O} \\
\mid \\
-\mathrm{CHX-C-CHX-C-} \\
\mid \qquad\qquad /\ \backslash \\
\mathrm{O} \qquad \mathrm{O} \quad \mathrm{O} \\
\mid \qquad\qquad \backslash\ / \\
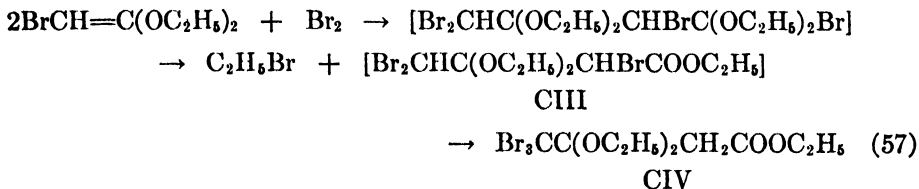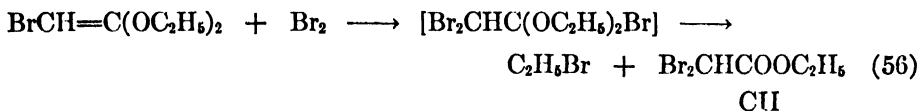\qquad\qquad\quad (\mathrm{CH_2})_n
\end{array}
$$

CI

Qualitatively, the dioxalanes of table 1 appear to polymerize more readily than the dioxanes, and the chloro compounds more readily than the bromo compounds. In fact, there is no noticeable difference in the ease with which the chloromethylenedioxolane (No. 29) and the unsubstituted methylenedioxolane (No. 7) undergo spontaneous polymerization. This is in marked contrast to the great difference in the polymerization behavior of ketene and chloroketene diethylacetals noted previously. The dimethylacetals of table 1 show approximately the same tendency to polymerization as the diethylacetals. The unsubstituted dimethylacetals may be induced to polymerize by acidified glass surfaces, cadmium chloride, and other catalysts that are able to coördinate with the anionoid center of the acetal. Chloroketene dimethylacetal shows the same resistance to polymerization (19) that was observed for the corresponding diethylacetal (12).

It is of interest to note that hydrogen chloride, which adds to the other cyclic acetals to yield ω-chloroalkyl esters (cf. addition of water in reaction 27), causes an anomalous polymerization of 2-methylene-1,3-dioxolane (19) similar to that which hydrogen fluoride causes with ketene diethylacetal (26, 27).

G. MISCELLANEOUS REACTIONS

1. With bromine

Although all of the ketene acetals readily absorb bromine, the exact course of this reaction has been determined only in the case of bromoketene diethylacetal (35). This ketene acetal absorbs bromine rapidly at 0–5°C. but the absorption stops abruptly after 0.7 of an equivalent of bromine has reacted. The products isolated from this reaction indicate that approximately one-half of the bromine reacts with a single molecule of the acetal, as shown in reaction 56, to yield ethyl dibromoacetate (CII), while the other half adds across two molecules of the acetal (reaction 57), in the 1,4 manner of reaction 32, to yield initially the α,γ,γ-tribromoacetoacetic ester diethylketal (CIII), which then rearranges to ethyl γ,γ,γ-tribromoacetoacetate diethylketal (CIV), the product actually isolated from reaction 57.

$$\mathrm{BrCH{=}C(OC_2H_5)_2 \ + \ Br_2 \ \longrightarrow \ [Br_2CHC(OC_2H_5)_2Br] \ \longrightarrow}$$

$$\mathrm{C_2H_5Br \ + \ Br_2CHCOOC_2H_5} \quad (56)$$
$$\mathrm{CII}$$

$$\mathrm{2BrCH{=}C(OC_2H_5)_2 \ + \ Br_2 \ \rightarrow \ [Br_2CHC(OC_2H_5)_2CHBrC(OC_2H_5)_2Br]}$$

$$\mathrm{\rightarrow \ C_2H_5Br \ + \ [Br_2CHC(OC_2H_5)_2CHBrCOOC_2H_5]}$$
$$\mathrm{CIII}$$

$$\mathrm{\rightarrow \ Br_3CC(OC_2H_5)_2CH_2COOC_2H_5} \quad (57)$$
$$\mathrm{CIV}$$
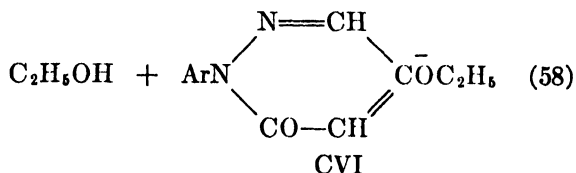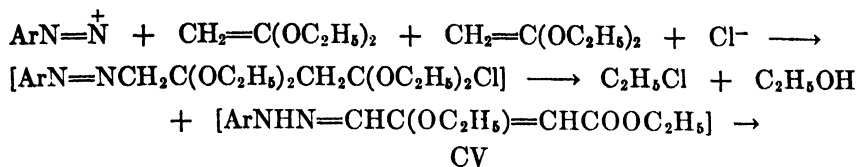
In addition to the main reaction products (CII and CIV), small and practically equivalent amounts of ethyl tribromoacetate and ethyl γ,γ-dibromoacetoacetate diethylketal, which result from the bromination of CII by CIII, are obtained from these reactions.

2. With diazonium salts

A study of the reaction of phenyl-, p-ethoxyphenyl-, p-nitrophenyl-, and p-carbethoxyphenyl-diazonium chlorides with ketene acetal has been made. As the acetal reacts with water and other hydroxylic solvents, these reactions were carried out with the dry salt in the presence of an excess of the ketene acetal (23).

In each case the main reaction product is a 1-aryl-4-ethoxy-6-pyridazone (CVI), the formation of which is rationalized as a cyclization of the hydrazone (CV) resulting from the addition of the diazonium salt across two molecules of the ketene acetal as shown in reaction 58. The yields of the pyridazones (CVI) are 25–35 per cent of the theoretical and it is of interest to note that the yields drop to approximately one-half of these values in each case if the reaction is carried out in pyridine, in which both reactants are soluble.

In addition to CVI, smaller quantities of diarylformazyl formates (CVII), which result from the initial addition of the diazonium salt to a single molecule

$$ArN\!=\!\overset{+}{N} \;+\; CH_2\!=\!C(OC_2H_5)_2 \;+\; CH_2\!=\!C(OC_2H_5)_2 \;+\; Cl^- \longrightarrow$$

$$[ArN\!=\!NCH_2C(OC_2H_5)_2CH_2C(OC_2H_5)_2Cl] \longrightarrow C_2H_5Cl \;+\; C_2H_5OH$$

$$+\; [ArNHN\!=\!CHC(OC_2H_5)\!=\!CHCOOC_2H_5] \rightarrow$$
$$CV$$

$$C_2H_5OH \;+\; ArN \overset{\displaystyle N=CH}{\underset{\displaystyle CO-CH}{\diagup \hspace{1cm} \diagdown}} \overset{\bar{}}{COC_2H_5} \quad (58)$$
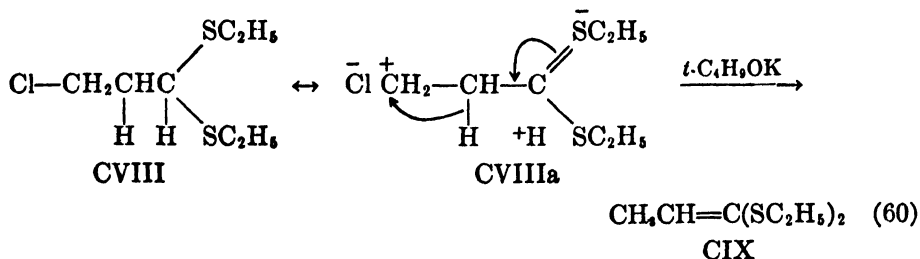$$CVI$$

of the ketene acetal followed by the subsequent reactions shown in reaction 59, are obtained in certain cases. The yields of CVII vary from zero when Ar is phenyl to 27 per cent when Ar is p-ethoxyphenyl.
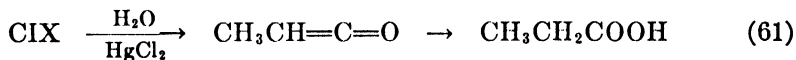
$$ArN\!=\!N^+Cl^- \;+\; CH_2\!=\!C(OC_2H_5)_2 \rightarrow [ArN\!=\!NCH_2C(OC_2H_5)_2Cl] \rightarrow$$

$$C_2H_5Cl \;+\; ArNHN\!=\!CHCOOC_2H_5 \xrightarrow{\;ArN\!=\!NCl\;}$$

$$\underset{\displaystyle ArN\!=\!N}{\overset{\displaystyle ArNHN\!=\!CCOOC_2H_5}{\underset{\displaystyle |}{\big|}}} \;+\; HCl \quad (59)$$
$$CVII$$
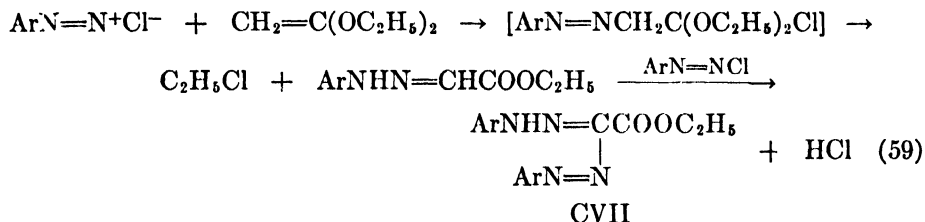
IV. SULFUR AND NITROGEN ANALOGS OF THE KETENE ACETALS

A. KETENE THIOACETALS

One example of a ketene thioacetal appears in the literature and its formation is of exceptional interest. The action of potassium t-butoxide on β-chloropropionaldehyde diethylthioacetal (CVIII) yields methylketene diethylthioacetal (CIX) in 77 per cent yield. This unusual dehydrohalogenation is the result of the ability of sulfur to expand its valence shell to permit the existence of the resonance form CVIIIa, which, in the presence of the strongly basic t-butoxy anions, undergoes dehydrohalogenation followed by the hydride ion and electron shifts shown in reaction 60. That CIX does not result from the initial formation of the isomeric acrolein diethylthioacetal, $CH_2\!=\!CHCH(SC_2H_5)_2$, is shown by the fact that both the latter compound and CIX are stable and not interconvertible under the conditions of reaction 60 (41).

$$\underset{\displaystyle CVIII}{Cl\!-\!CH_2CHC\overset{\displaystyle SC_2H_5}{\underset{\displaystyle \underset{H\ H}{|\ |}\ SC_2H_5}{\diagup \diagdown}}} \quad \leftrightarrow \quad \underset{\displaystyle CVIIIa}{\bar{Cl}\ \overset{+}{C}H_2\!-\!\underset{\displaystyle \underset{H}{|}}{CH}\!-\!C\overset{\displaystyle \bar{S}C_2H_5}{\underset{\displaystyle {}^+H\ \ SC_2H_5}{\diagup \diagdown}}} \quad \xrightarrow{\;t\text{-}C_4H_9OK\;}$$

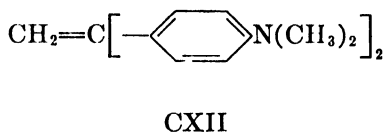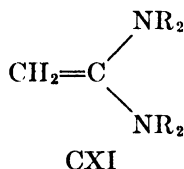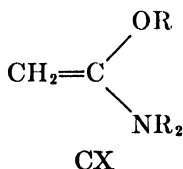$$CH_3CH\!=\!C(SC_2H_5)_2 \quad (60)$$
$$CIX$$

The structure of the ketene thioacetal (CIX) is shown by its conversion to propionic acid with an aqueous solution of mercuric chloride (reaction 61). Methylketene is postulated as an intermediate in this reaction (41).

$$\text{CIX} \xrightarrow[\text{HgCl}_2]{\text{H}_2\text{O}} \quad \text{CH}_3\text{CH}=\text{C}=\text{O} \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{COOH} \qquad (61)$$

B. NITROGEN ANALOGS OF THE KETENE ACETALS

There are two types of these nitrogen analogs: CX, in which a disubstituted nitrogen replaces one of the alkoxyl groups of a ketene acetal, and CXI, in which both of the alkoxyl groups are so replaced. These compounds are of interest because the presence of the more effective hetero atom, nitrogen, in the heteroenoid system of such compounds would be expected to enhance the reactivity of the methylene carbon. Such a supposition is supported by the observation of Gates (10) that 1,1-bis(p-dimethylaminophenyl)ethylene (CXII), which may be considered a vinylog of CXI, is much more reactive with certain quinones than is the analogous 1,1-dianisylethylene, which is a vinylog of ketene dimethylacetal.

$$\text{CH}_2=\text{C}\begin{array}{c}\diagup \text{OR} \\ \diagdown \text{NR}_2\end{array} \qquad \text{CH}_2=\text{C}\begin{array}{c}\diagup \text{NR}_2 \\ \diagdown \text{NR}_2\end{array} \qquad \text{CH}_2=\text{C}\left[-\!\!\left\langle\underline{\quad}\right\rangle\!\!\text{N(CH}_3)_2\right]_2$$

$$\quad\quad\text{CX}\qquad\qquad\qquad\text{CXI}\qquad\qquad\qquad\qquad\text{CXII}$$

The preparation of a compound of type CX, N-ethyl-N-(α-ethoxyvinyl)-aniline (LVI), is described in reaction 37 of Section III B. Hydrolysis converts LVI to ethylaniline, alcohol, and acetic acid; all attempts to stop the hydrolysis at the N-ethylacetanilide stage have been unsuccessful. LVI dissolves exothermically in alcohol but distillation of the solution returns LVI unchanged (32).

The preparation of a compound of type CXI was attempted by the pyrolysis of 1,1,1-tripiperidinoethane (LVII), which is obtained from reaction 39. This ethane is remarkably stable to heat—it boils at 255–258°C. without decomposition—but when it is refluxed vigorously over a period of 9 hr., approximately 89 per cent of the theoretical quantity of piperidine slowly distils from it. However, the remaining product is polymeric, indicating either that the loss of piperidine is intermolecular or that the 1,1-dipiperidinoethylene, resulting from the intramolecular loss of piperidine, is polymerized during the long period of pyrolysis (32).

In contrast to the behavior of piperidine in reaction 39, diethylamine and di-n-butylamine react with ketene diethylacetal at 120–130°C. to give products of types CX and CXI in 13–16 per cent and 34–41 per cent yields, respectively. The amount of ethyl orthoacetate accompanying these amino compounds indicates that the molecular ratios of reactants shown in reactions 62 and 63 are required (32).

It is apparent from the ratios of reactants required for these reactions that the rate of addition of the amine to the ketene acetal is much lower than that

$$2CH_2=C(OC_2H_5)_2 \ + \ R_2NH \ \rightarrow$$

$$CH_3C(OC_2H_5)_3 \ + \ CH_2=C(OC_2H_5)NR_2 \quad (62)$$
$$CX$$

$$3CH_2=C(OC_2H_5)_2 \ + \ 2R_2NH \ \rightarrow \ 2CH_3C(OC_2H_5)_3 \ + \ CH_2=C(NR_2)_2 \quad (63)$$

R is C_2H_5 or $n\text{-}C_4H_9$. $\qquad\qquad\qquad\qquad\qquad\qquad$ CXI

at which alcohol adds to form the orthoester. The mechanism of these reactions appears to involve the initial addition of the amine to the acetal followed by a loss of alcohol (which converts an equivalent of the ketene acetal to the ortho-ester) to form CX; a repetition of this process converts CX to CXI. Evidence for this mechanism is obtained from the aminolysis of ethyl orthoacetate with the amines used in reactions 62 and 63. This aminolysis requires a temperature of 200–220°C., in contrast to the temperature of 120–130°C. used in reactions 62 and 63, and the reaction takes the course shown in reaction 64. The amide (CXV) is obtained in quantitative yields; this, together with the fact that the tertiary amine (CXIV) also is formed, indicates that the intermediate CXIII, at the higher temperature of reaction 64, preferentially pyrolyzes to CXIV and ethyl acetate rather than to alcohol and CX as it does in reaction 62 (32).

$$CH_3C(OC_2H_5)_3 \ + \ R_2NH \ \xrightarrow{220°C.}$$

$$C_2H_5OH \ + \ CH_3C(OC_2H_5)_2NR_2 \ \rightarrow$$
$$CXIII$$

$$C_2H_5NR_2 \ + \ CH_3COOC_2H_5 \ \xrightarrow{R_2NH} \ CH_3CONR_2 \quad (64)$$
$$CXIV \qquad\qquad\qquad\qquad\qquad\qquad CXV$$

The ethoxyaminoethylenes (CX) and the diaminoethylenes (CXI) show a considerable tendency to polymerize during distillation. Both types are basic and dissolve in dilute (5 per cent) aqueous acids; the CXI type is hydrolyzed to the corresponding amide and the secondary amine. Alcohol converts the diamino compounds (CXI) to the monoamino compounds (CX). Under the mildest conditions of hydrogen absorption (Raney nickel and 2100 p.s.i. of hydrogen at 60°C.) 1,1-bis(diethylamino)ethylene (CXI: R is C_2H_5) undergoes hydrogenolysis and yields a mixture of diethylamine and triethylamine (32).

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THE BEHAVIOR OF CONJUGATED SYSTEMS CONTAINING AROMATIC DOUBLE BONDS TOWARDS ORGANOMETALLIC REAGENTS

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CONTENTS

I. INTRODUCTION

Involvement of the double bonds of aromatic nuclei in reactions with Grignard reagents was first observed in 1929 by Gilman, Kirby, and Kinney (31) with benzophenone anil. Since that time similar results have been reported for aryl ketones and nitriles. In view of the considerable extent to which the field has been developed and the current interest in this type of reaction, a review of the progress that has been made seems timely.

It is the purpose of the present paper to present a survey of the work with Grignard reagents as well as with certain other organometallic compounds.

II. CONJUGATE ADDITION

A. 1,4-ADDITION

1. To systems containing the grouping —C=C—C=N—

(a) *Anils:* The report of Gilman, Kirby, and Kinney (31) involved benzophenone anil (I) and phenylmagnesium bromide. They observed the formation of *o*-phenylbenzohydrylaniline (II) and suggested that the reaction proceeded with the disruption and regeneration of the aromatic double bond. The same compound was obtained by allowing the Grignard reagent to act upon phenyl isocyanate or phenyl isothiocyanate and was synthesized unequivocally by the

C_6H_5C=NC_6H_5 $\xrightarrow[\text{90–105°C., 42\%}]{C_6H_5MgBr}$

$$C_6H_5\overset{\overset{\displaystyle MgBr}{|}}{C}NC_6H_5$$

$\xrightarrow[\text{rearrangement}]{H_2O}$

$C_6H_5CHNHC_6H_5$

II
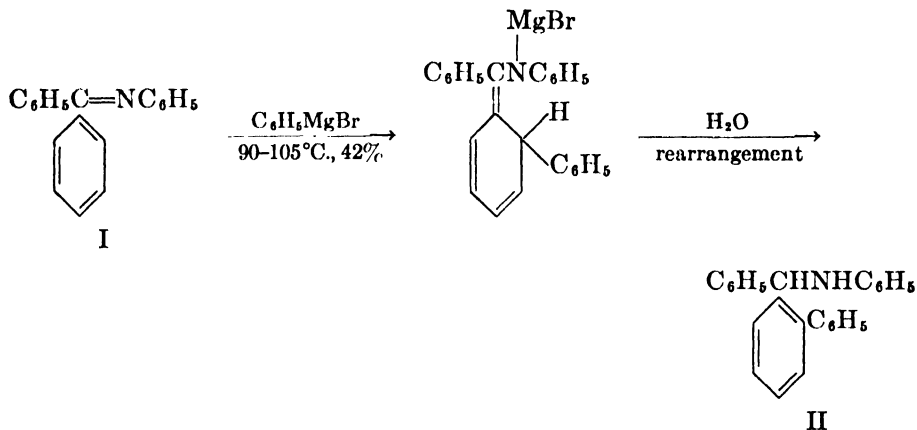
interaction of *o*-biphenylylmagnesium iodide and benzalaniline. Later benzophenone oxime was shown by Campbell and McKenna (8) to yield the same amine (II) on treatment with the phenyl Grignard reagent.

Very recently, Gilman and Morton (32) have shown that a similar course was taken in the "forced" addition of phenylmagnesium bromide to benzophenone β-naphthil (III); no reaction involving the naphthalene nucleus could be detected. The product (IV) was identical with that from the reaction of *o*-biphenylyl magnesium iodide with benzal-β-naphthylamine (V).

N=$C(C_6H_5)_2$ $\xrightarrow[\text{90–100°C., 71\%}]{C_6H_5MgBr}$

III

$β-C_{10}H_7NHCHC_6H_5$

C_6H_5

IV

$\xleftarrow{o\text{-}C_6H_5C_6H_4MgI}$ $β-C_{10}H_7N$=CHC_6H_5

V
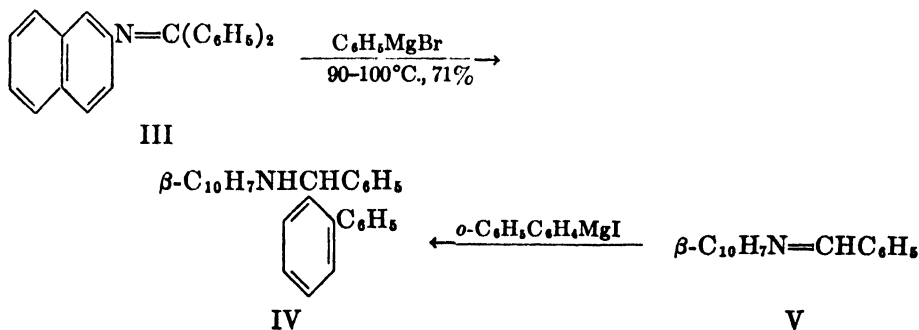
(b) *Heterocycles:* A slightly different type of activation by a hetero atom has been observed to result in 1,4-addition to a ring–chain system. Hoffman, Farlow, and Fuson (34) added phenylmagnesium bromide to benzalquinaldine (VI) and *p*-chlorobenzalquinaldine (VIII) to give α-benzohydrylquinaldine (VII) and the *p*-chloro analog (IX), respectively. The first product was also obtained by the addition of benzene in the presence of aluminum chloride. This compound (VII) has recently been obtained by Gilman and Gainer (30a) in quantitative yield from benzalquinaldine by the action of phenyllithium.
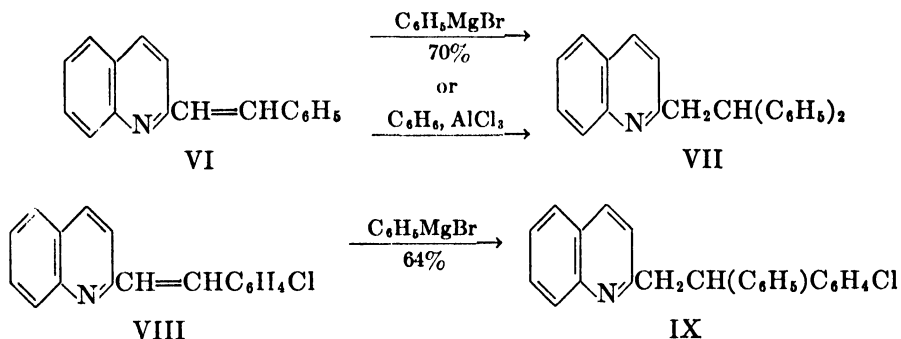
Recently the addition of the *n*-propyl Grignard reagent to nicotinonitrile (X) has been observed to yield *n*-propyl 4-*n*-propyl-3-pyridyl ketone (XI) (12). It may be pointed out that the probable intermediate would be capable of resonance.
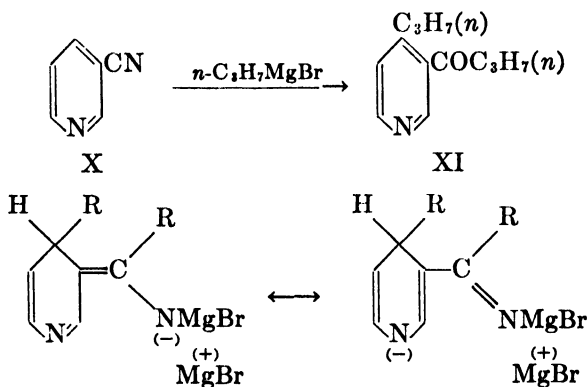
Acridine and quinoline also contain the system —C=C—C=N—, and several authors have investigated the addition of organometallic reagents to this type of compound. It was reported by Freund (13) in 1904 that the reaction of acridine methiodide (XII) with ethylmagnesium iodide yielded 9-ethyl-10-methyl-9-phenyl-9,10-dihydroacridine (XIII). Later Bergmann, Blum-Bergmann, and von Christiani (6) allowed acridine itself to react with phenylmagnesium bromide and aryllithium compounds. The primary product in all cases was the corresponding 9-aryl-9,10-dihydroacridine (XIV), although this was partially converted to the

aromatic compound by "secondary oxidation" in the case of reaction with the Grignard reagent. Ziegler and Zeiser (51) also found that butyllithium added similarly to acridine, and that quinoline reacted with either this reagent or

$$C_6H_5 \qquad \xrightarrow{C_2H_5MgI} \qquad C_2H_5 \quad C_6H_5$$

XII   XIII

$$\xrightarrow[\text{or } C_6H_5MgBr]{ArLi} \qquad \xrightarrow{H_2O}$$

XIV
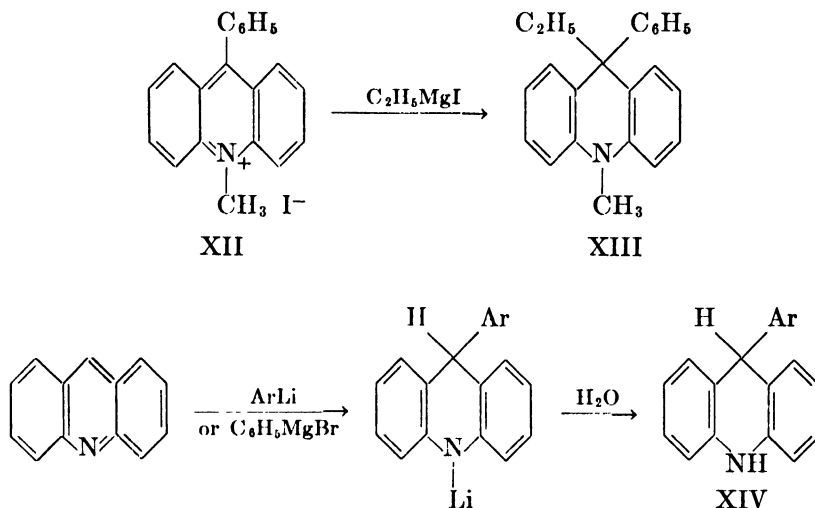
Ar = C_6H_5, p-$CH_3OC_6H_4$, o- and m-$CH_3C_6H_4$, α-$C_{10}H_7$.

phenyllithium to give a small amount of the corresponding 4-substituted compound isolated as the picrate, as well as the normal 2-substituted compound. Similar results were reported by Bergmann and Rosenthal (7), who used benzylmagnesium chloride. Acridine gave the expected products; quinoline was reported

$$\xrightarrow{RLi}$$
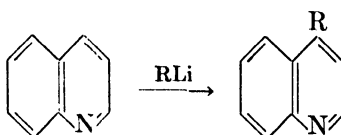
R = n-C_4H_9, C_6H_5.

to give both the 4-benzyl (XV) and the 2,4-dibenzyl (XVI) derivative, in addition to the 2-benzyl derivative. In view of the recent reports that phenyllithium adds in the 1,2 manner to 2-phenylquinoline (30), the identity of the dibenzylquinoline might be questioned. Bergmann and Rosenthal also reported the 1,4-
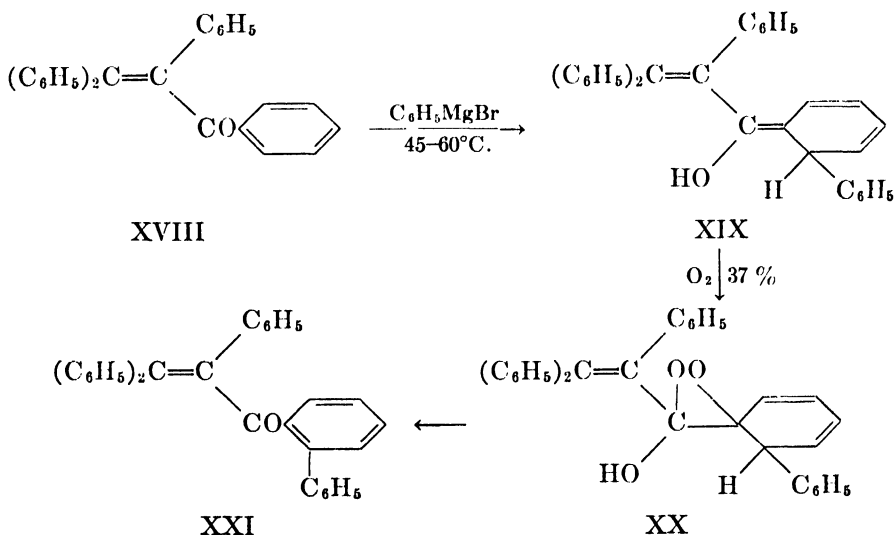
$$\xrightarrow{C_6H_5CH_2MgCl} \qquad CH_2C_6H_5 \qquad + \qquad CH_2C_6H_5$$

$$CH_2C_6H_5$$

XV   XVI
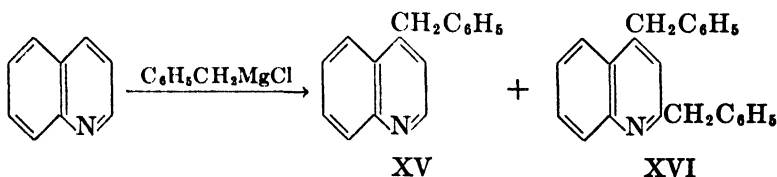
addition of benzhydrylsodium to acridine, the product being 9-benzhydryl-
9,10-dihydroacridine (XVII).
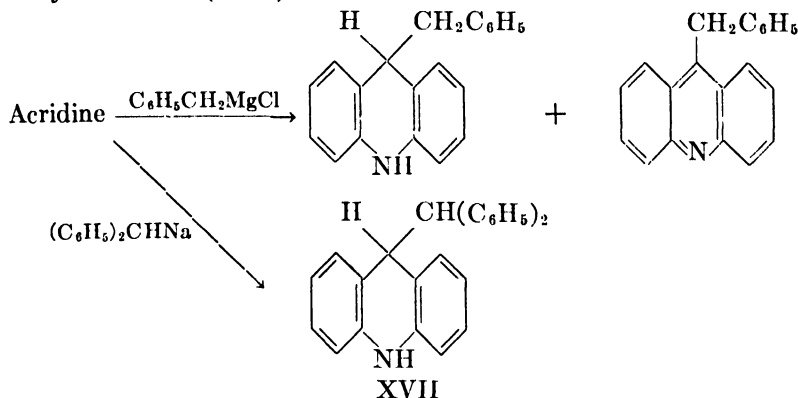
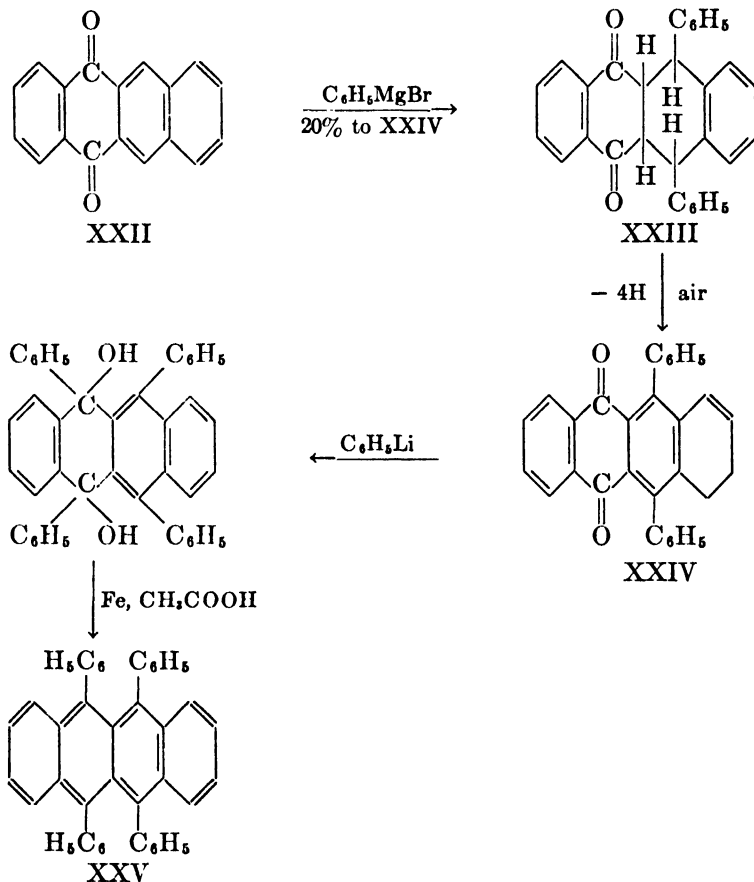*2. To systems containing the grouping* $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$

(a) *Polycyclic ketones:* o-Arylation of an aromatic ketone was first observed by
Kohler and Nygaard (43), who treated the α,β-ethylenic compound XVIII with
the phenyl Grignard reagent and found to their surprise that the reaction in-

volved not the extracyclic unsaturation but a double bond in an aromatic ring.
They isolated the peroxide (XX) of the enol (XIX) in 37 per cent yield and de-
composed it to the corresponding aromatic ketone (XXI), from which by oxidative
cleavage were obtained benzophenone and o-phenylbenzil.

This type of addition was soon extended to fused polycyclic systems. Almost
simultaneously Allen and Gilman (1) and Dufraisse and Horclois (11) announced
the double 1,4-addition of phenylmagnesium bromide to naphthacenequinone

(XXII). The resulting stereoisomeric tetrahydro ketones (XXIII) were converted to rubrene (XXV) by the former workers, whose formulations are shown. It is of interest that the intermediate 6,11-diphenyl-5,12-naphthacenequinone (XXIV) was unaffected by the phenyl Grignard reagent but added phenyllithium
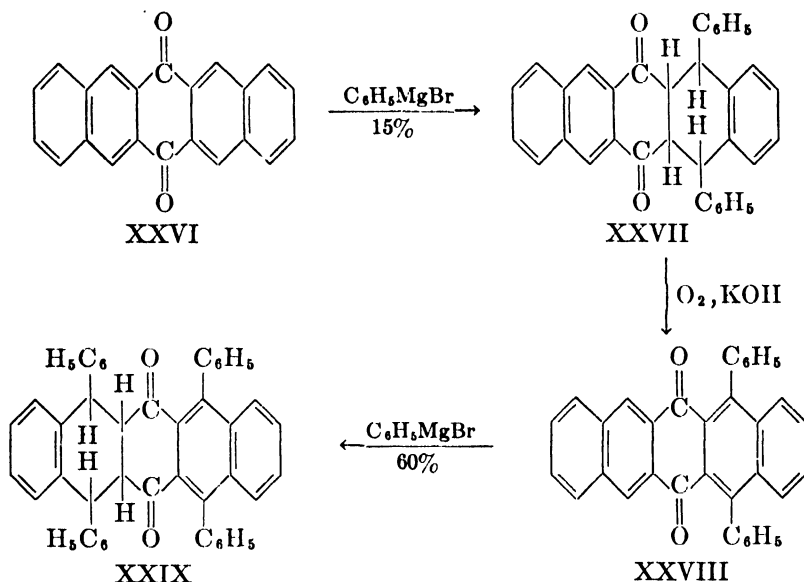
$$\text{XXII} \xrightarrow[20\% \text{ to XXIV}]{C_6H_5MgBr} \text{XXIII}$$

XXIII $\xrightarrow[\text{air}]{-4H}$ XXIV

XXIV $\xleftarrow{C_6H_5Li}$ (C$_6$H$_5$, OH, C$_6$H$_5$ diol)

diol $\xrightarrow{\text{Fe, CH}_3\text{COOH}}$ XXV

readily. This compound (XXIV) was also converted by fusion with potassium hydroxide to benzoic and 1,4-diphenyl-2-naphthoic acids, a proof of the double 1,4-addition.

Quite similar results were obtained by Allen and Bell (2) with 6,13-pentacenequinone (XXVI). This compound reacted with phenylmagnesium bromide to give as the major product (70 per cent) the normal diol; however, the tetrahydro ketone (XXVII) resulting from a double 1,4-addition was also isolated. Oxidation of the compound gave the fully aromatic 5,14-diphenyl-6,13-pentacenequinone (XXVIII), which was also found to undergo a similar double conjugate addition of the same reagent to give a second tetrahydro ketone (XXIX).

Another example of a fused polynuclear ketone which undergoes 1,4-addition of Grignard reagents is benzanthrone (XXX). Both Clar (10) and Nakanishi (45) obtained what they believed to be a 1,6-addition product with the phenyl
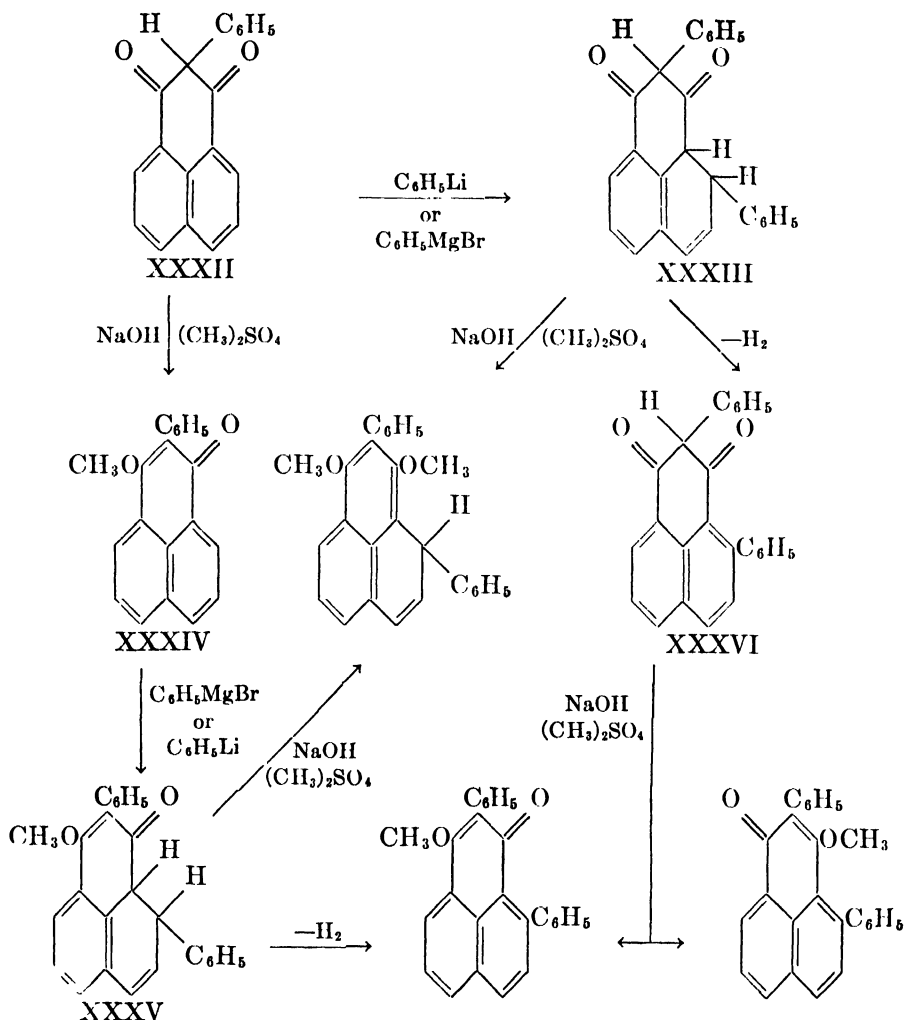
Grignard reagent, but these claims have been disproved (4, 9). Charrier and Ghigi (9) did show that the methyl and ethyl reagents added in the 1,4 manner.

The reaction of benzanthrone with Grignard reagents was later investigated more exhaustively by Allen and Overbaugh (3), who showed that the reaction took the following path:

R = C_6H_5 (42%), $C_6H_5CH_2$ (22%),
     n-C_6H_{13} (61%), cyclo-C_6H_{11} (15%).
R′ = C_6H_5, C_6H_5CO.

They considered their failure to isolate dihydro compounds as due probably to simultaneous oxidation and reduction, stating that yields were in accord with this assumption and that tarry by-products of these reactions might be converted to additional amounts of the substitution products by treatment with quinone. Only the *t*-butyl Grignard reagent added to the ketone in the 1,2 manner, as it did to an analog, *bz*-1-phenylbenzanthrone (XXXI). These authors found an indication of the generality of the conjugate addition by examining the behavior of the latter compound with other Grignard reagents (4).

R = $C_6H_5CH_2$ (19%), C_6H_5 (45%),
      $C_6H_5CH_2CH_2$ (51%), cyclo-C_6H_{11} (22%),
      C_2H_5 (35%), n-C_4H_9 (53%), n-C_6H_{13} (47%),
      $C_6H_5CH{=}CH$ (6%).

A compound which possesses the affected portion of the structure of benzanthrone is 8-phenyl-*peri*-naphthindandione-7,9 (XXXII). This and a related substance (XXXIV) have been found by Koelsch and Rosenwald (41) to undergo 1,4-addition of both the Grignard reagent and phenyllithium. These and related reactions of the products are given on page 501.

The transformation of XXXII to XXXIII proceeded in good yield with phenyllithium, but only small yields were isolated with phenylmagnesium bromide; the reverse was true of the change of XXXIV to XXXV. 1,8-Diphenyl-*peri*-naphthindandione-7,9 (XXXVI) was oxidized to 2-phenylnaphthalic anhydride, which underwent ring closure and decarboxylation to the known 1,2-benzofluorenone.

Another example of conjugate addition to this type of system was found by Koelsch and Rosenwald (42) in 7-ethoxy-*peri*-naphthindenone-9 (XXXVII), which was shown to add phenylmagnesium bromide in the 1,4 manner.

H C_6H_5
O O

XXXII

$\xrightarrow{\begin{array}{c} C_6H_5Li \\ \text{or} \\ C_6H_5MgBr \end{array}}$

H C_6H_5
O O
—H
—H
C_6H_5

XXXIII

NaOH | $(CH_3)_2SO_4$

NaOH / $(CH_3)_2SO_4$ —H₂

C_6H_5 O
CH_3O

XXXIV

C_6H_5
CH_3O OCH_3
II
C_6H_5

H C_6H_5
O O
C_6H_5

XXXVI

C_6H_5MgBr
or
C_6H_5Li

NaOH
$(CH_3)_2SO_4$

NaOH
$(CH_3)_2SO_4$

C_6H_5 O
CH_3O
H
H
C_6H_5

XXXV

—H₂ →

C_6H_5 O
CH_3O
C_6H_5

O C_6H_5
OCH_3
C_6H_5

This study was extended by Geissman and Morris (29) to 8,8-dimethyl-*peri*-naphthindandione-7,9 (XXXIX), which underwent simultaneous 1,2- and 1,4-addition of two molecules of the phenyl reagent. Under milder conditions compounds resulting from either single or double normal addition could be obtained as the major product.

Similar behavior was later observed by Koelsch and Anthes (40) with the simpler *peri*-naphthenone-7 (XL). The enolic (phenolic) dihydro intermediate was dehydrogenated by distillation at reduced pressure to give 1-phenyl-*peri*-naphthenone-7 (XLI), which was also oxidized to 2-phenylnaphthalic anhydride. It is to be noted that, in this example of 1,4-addition, reaction occurred with an aromatic double bond rather than with the apparently simple ethylenic linkage between the 8 and 9 positions.
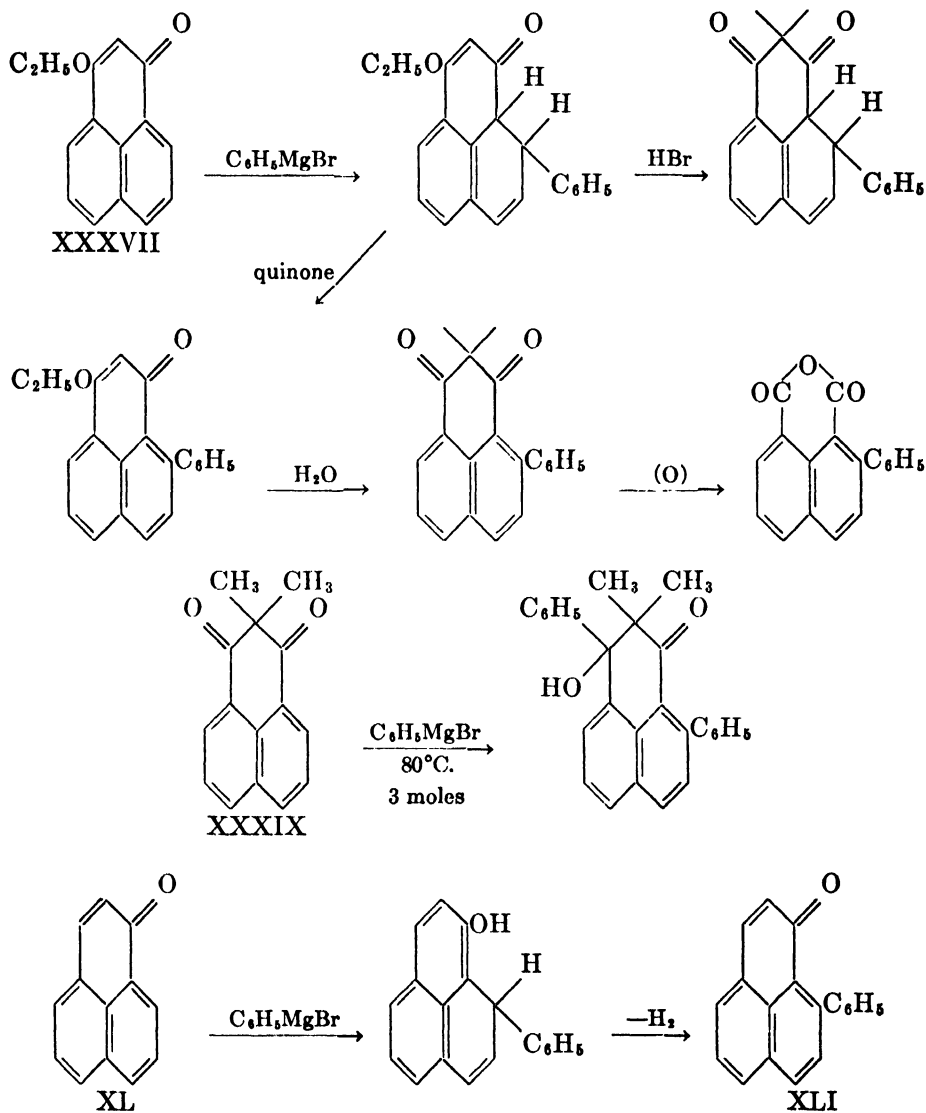
(b) *Simple hindered diaryl ketones: i. Involving the furan nucleus*—There are
two examples in which conjugate addition of a Grignard reagent disrupted a furan
nucleus. Although 2-benzoylbenzofuran adds these reagents in the normal 1,2
manner, Fuson, Kaiser, and Speck (22) used the hindering effect of the mesityl
(Mes or 2,4,6-trimethylphenyl) and tipyl (Tip or 2,4,6-triisopropylphenyl)
radicals to suppress this course with mesityl 2-benzofuryl (XLII) and tipyl
2-benzofuryl (XLIII) ketones and obtained the corresponding 2-aroyl-3-phenyl-
2,3-dihydrobenzofurans (XLV). If the intermediate enols were treated with

oxygen, the resulting enol peroxides decomposed to yield, in both cases, 3-phenyl-isocoumaranone (XLIV) as well as mesitoic or triisopropylbenzoic acid.

$$\underset{\text{XLII: Ar = Mes}}{\underset{\text{XLIII: Ar = Tip}}{\text{(structure) COAr}}} \xrightarrow{C_6H_5MgBr} \text{(structure) } C_6H_5 \text{ OMgBr}$$

$$ArCOOH \; + \; \underset{XLIV}{\text{(structure) } C_6H_5} \qquad \underset{XLV}{\text{(structure) } C_6H_5}$$
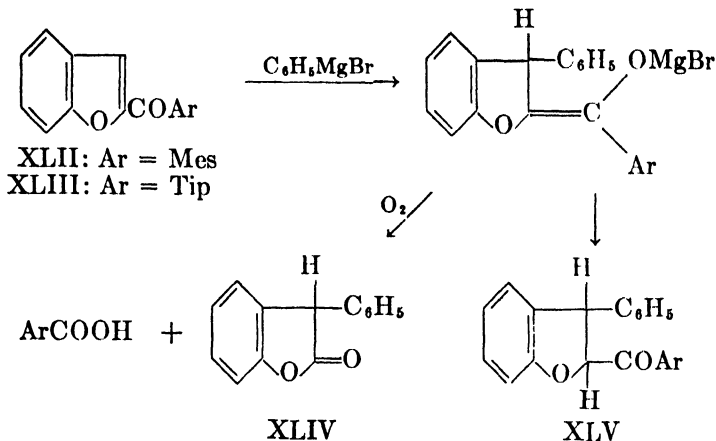
Lutz and Reveley (44) treated 3-mesitoyl-5-mesityl-2-methyl-4-phenylfuran (XLV) with methylmagnesium iodide and obtained the product which would result by a process of 1,4-addition followed by fission of the ether linkage, 2-*t*-butyl-1,4-dimesityl-3-phenyl-1,4-butanedione (XLVI). This compound was prepared by two independent methods,—hydrogenation of the corresponding butene and 1,4-addition of phenylmagnesium bromide to 2-*t*-butyl-1,4-dimesityl-2-butene-1,4-dione (XLVII).

$$\underset{XLV}{\overset{C_6H_5 \quad COMes}{\underset{Mes \quad O \quad CH_3}{\text{(structure)}}}} \xrightarrow{CH_3MgI} \overset{OMgI}{\underset{Mes \quad O \quad CH_3}{C_6H_5 \quad CH_3 \quad C \diagdown Mes}} \xrightarrow{etc.}$$

$$\overset{OMgI}{\underset{\overset{|}{O}MgI}{C_6H_5C - C = C \diagdown Mes}} \\ \underset{MesC \quad C(CH_3)_3}{}$$

$$H_2O \downarrow\uparrow CH_3MgI$$

$$\underset{\overset{|}{C}(CH_3)_3}{MesCOCH=CCOMes} \xrightarrow{C_6H_5MgBr} \underset{\overset{|}{C_6H_5} \quad \overset{|}{C}(CH_3)_3}{MesCOCH——CHCOMes}$$

$$\quad\quad\quad\quad XLVII \quad\quad\quad\quad\quad\quad\quad\quad\quad XLVI$$
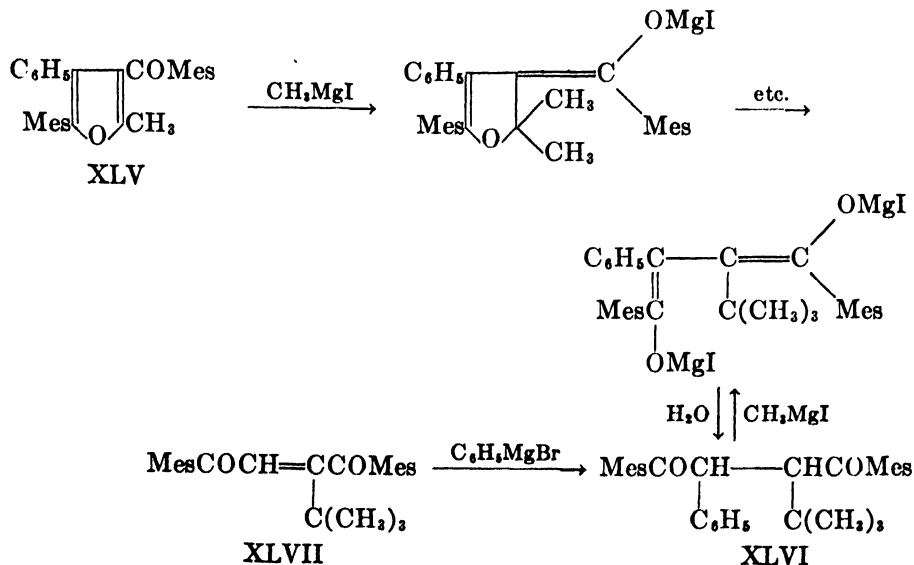
ii. Involving benzenoid nuclei—This use of steric hindrance to prevent the 1,2-addition of Grignard reagents while still retaining the powerful activating effect

of the carbonyl group has proved extremely fruitful, leading to the discovery of a number of examples of the conjugate addition of organometallic compounds into aromatic nuclei. Fuson, Botorff, Foster, and Speck (16, 17) investigated the reaction of esters of mesitoic acid with Grignard reagents. With alkyl mesitoates
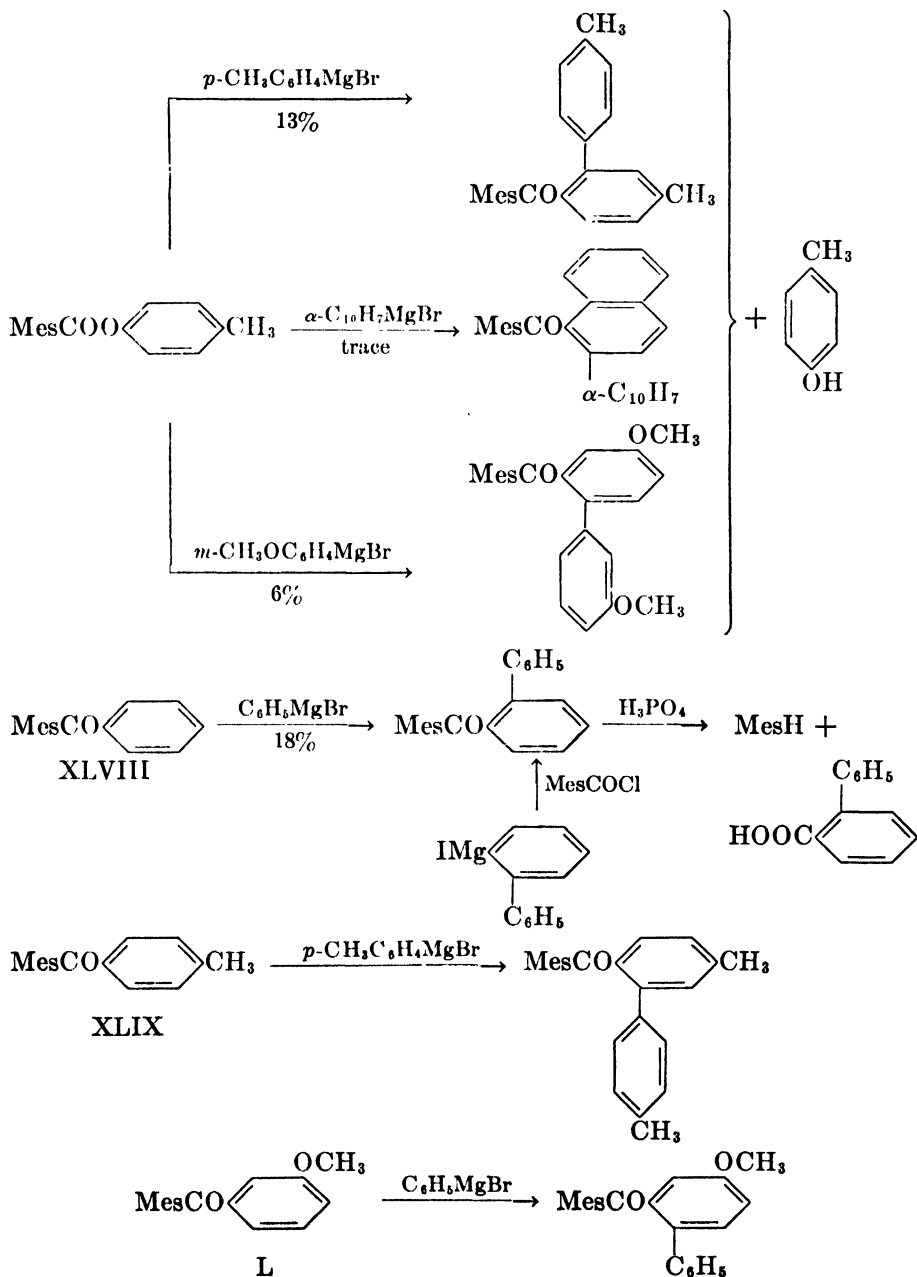
only cleavage resulted; aryl esters, however, gave with aryl reagents the products resulting from 1,4-addition to the supposedly intermediate ketones. The yields of *p*-cresol varied from 40 to 95 per cent. With a hindered Grignard reagent,
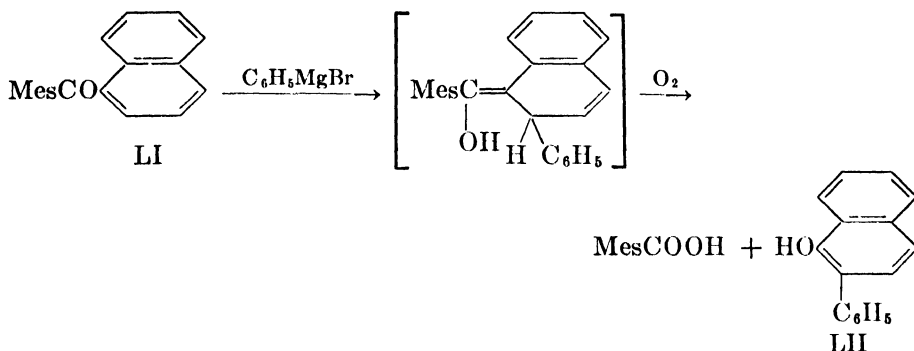
mesitylmagnesium bromide, only small amounts of dimesityl ketone and mesitil were isolated. These observations led logically to the use of the mesityl ketones themselves (14). Mesityl phenyl ketone (XLVIII), mesityl *p*-tolyl ketone (XLIX), and mesityl *m*-methoxyphenyl ketone (L) reacted to give the *o*-arylated ketones. In the first case the structure of the product was proved by synthesis from 2-biphenylylmagnesium iodide and by cleavage with acid to *o*-phenyl-benzoic acid. Mesityl 1-naphthyl ketone (LI) formed an intermediate enol which was cleaved by air to 2-phenyl-1-naphthol (LII) and mesitoic acid. This ketone
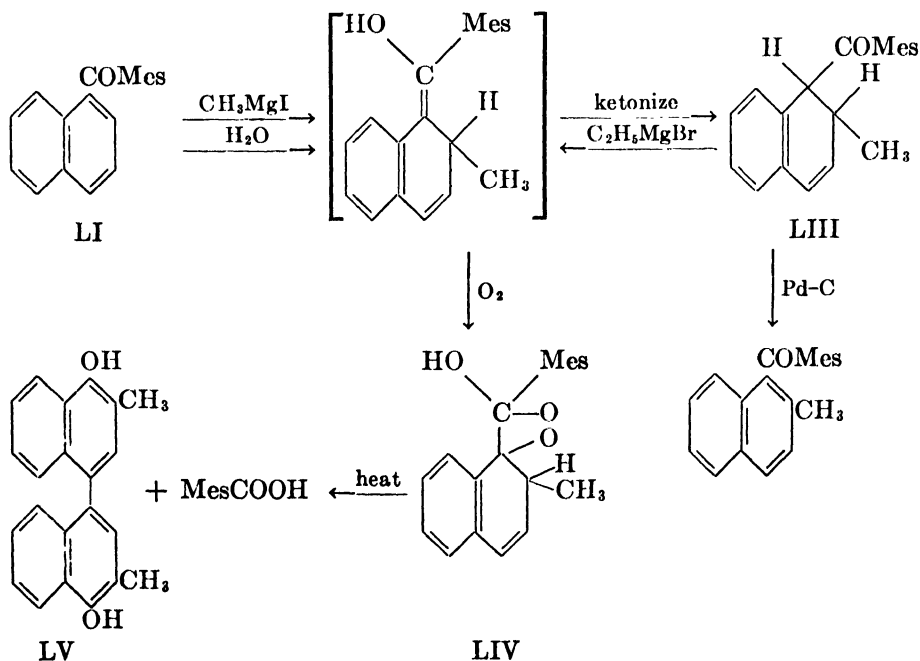
(LI) was also treated with methylmagnesium iodide by Fuson, McKusick, and Spangler (25), who showed that dihydro ketones are probably intermediates in many similar reactions by isolating such compounds. They are quite stable in these cases and some of their more interesting reactions are shown in the diagram. 1,2-Dihydro-1-mesitoyl-2-methylnaphthalene (LIII) formed an acetate from which it could be regenerated by hydrolysis and liberated one mole of methane in the Grignard machine. This suggested that the enol was quite stable, and it was treated with oxygen to form a crystalline peroxide (LIV) which decomposed to the known 4,4'-dihydroxy-3,3'-dimethyl-1,1'-dinaphthol (LV).

A similar series of transformations was observed with the isomeric mesityl 2-naphthyl ketone (LVI), the yield of 74 per cent in one run being one of the highest ever observed in a Grignard reaction involving an aromatic nucleus.
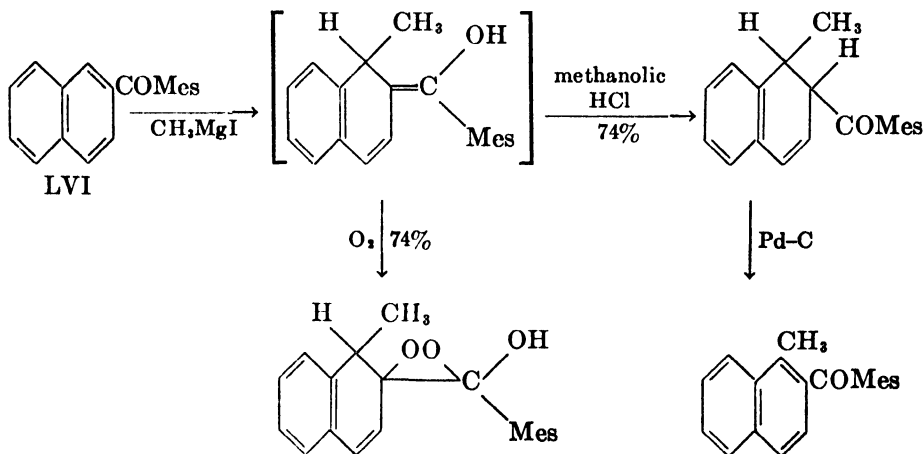
It is interesting that this type of steric hindrance is not always effective in preventing normal addition. Fuson and Robertson (26) first observed 1,2-addition to a mesityl ketone, in this case t-butyl mesityl diketone (LVII), which added the methyl Grignard reagent to give both possible products. Later Young and Roberts (50) observed this type of addition with s-butenylmagnesium bromide
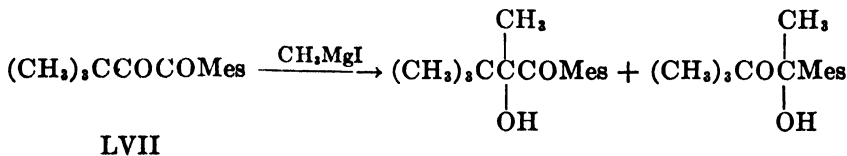
and benzylmagnesium chloride to acetomesitylene. Mesityl phenyl ketone (LVIII), isoduryl phenyl ketone (LX), and mesityl p-tolyl ketone (LIX) were
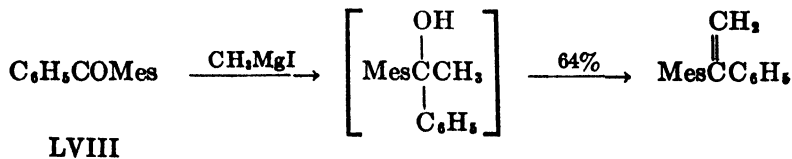
also found by Fuson, Armstrong, Wallace, and Kneisley (15) to form the corresponding ethylenes, presumably by dehydration of the intermediate carbinols.

$$CH_3 \bigcirc COMes \xrightarrow{CH_3MgI} CH_3 \bigcirc \overset{CH_2}{\underset{\parallel}{C}} Mes$$

LIX

$$\overset{H_3C \quad CH_3}{C_6H_5CO} \bigcirc \overset{CH_3}{\underset{H_3C}{}} \xrightarrow{CH_3MgI} \overset{H_2C}{C_6H_5C} \overset{H_3C \quad CH_3}{\bigcirc} \overset{CH_3}{\underset{H_3C}{}}$$

LX
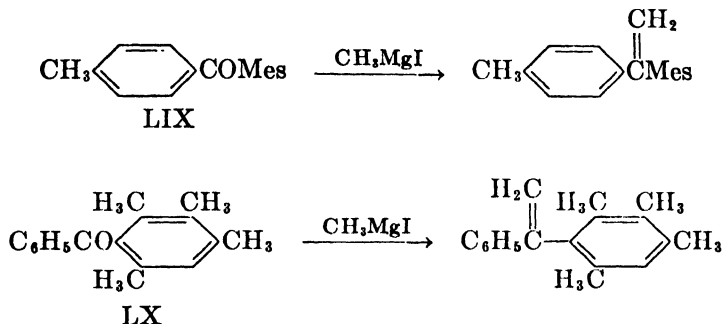
Two examples of the 1,4-addition of phenyllithium have already been mentioned. With this reagent the use of a hindering radical, e.g., mesityl, is less effective than in the case of the Grignard reagent, but with p-anisyl duryl ketone (LXI) and m-anisyl mesityl ketone (LXII) 1,4-addition was observed (20). The product of the latter reaction was identical with that previously obtained by the action of phenylmagnesium bromide (27). Strangely enough, mesityl 3,4-dimethoxyphenyl ketone (LXIII) and mesityl 2-methoxy-5-methylphenyl ketone (LXIV) yielded only the products of 1,2-addition, illustrating the strong tend-

CODur   H   CODur   CODur
  | \|/ | | C_6H_5
  | $\xrightarrow{C_6H_5Li}$ | C_6H_5 $\xrightarrow{-H_2}$ |
  | | |
 OCH_3   OCH_3   OCH_3
LXI   OCH_3   OCH_3

COMes   COMes
  | | C_6H_5
CH_3O | $\xrightarrow{C_6H_5Li}$ CH_3O |
LXII

COMes   COMes
  | | OCH_3
  | OCH_3   H_3C |
 OCH_3
LXIII   LXIV
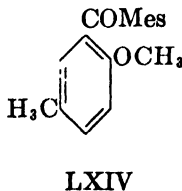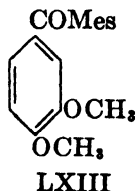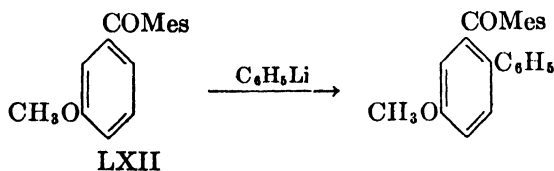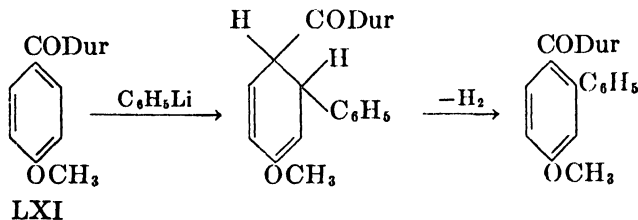
ency of phenyllithium to react in this manner.

Other examples of 1,4-addition to aromatic systems will be discussed later (page 515 ff.) in connection with the replacement of functional groups.

B. 1,6-ADDITION

1. To fuchsones

Claims of 1,6-addition of the Grignard reagent to aromatic systems were first advanced by both Clar (10) and Nakanishi (45) in connection with the reaction of benzanthrone with the phenyl reagent. As has been mentioned, these examples have been shown to be cases of 1,4-addition (3). However, Nakanishi also claimed to have isolated anthrafuchsone (LXVI) from the reaction of "benzyl-ideneanthrone" or benzalanthrone (LXV) with this reagent. The reaction was subsequently investigated by Julian and Magnani (39) and by Julian and Cole (36), who were unable to duplicate these results. Only 1,2-adducts were isolated by these workers with the methyl and phenyl reagents (36, 37, 39). However, 1,6-addition was observed by Julian and coworkers with other fuchsone-like

R = CH₃, C₆H₅.
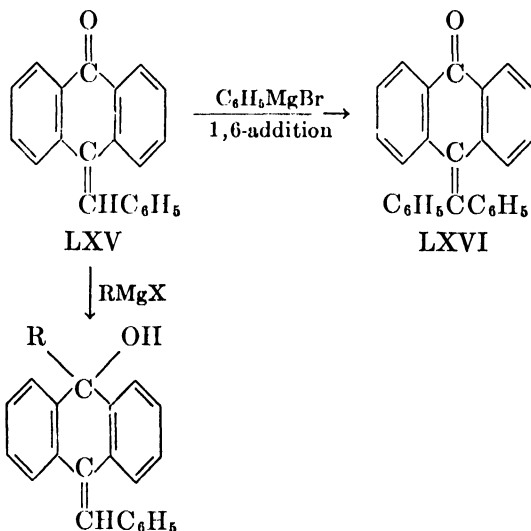
compounds. This reaction, although not resulting in substitution of a Grignard radical for hydrogen in an aromatic nucleus, is probably most accurately considered as involving addition to a system of which the "aromatic" ethylenic linkage between atoms 3 and 4 is a vital part. With methyleneanthrone (LXVII) the impure product was 10-benzylanthranol (LXVIII), characterized as a peroxide which decomposed into anthraquinone and benzyl alcohol (36, 39). The same peroxide was later synthesized by the simultaneous addition of hydrogen and oxygen to benzalanthrone (LXV) , while hydrogen alone gave the anthranol (LXVIII), which rearranged to 10-benzylanthrone (LXIX) (36). The methyl and ethyl reagents were also added to methyleneanthrone; the products, isolated as peroxides, similarly decomposed yielding ethyl and propyl alcohols, respectively. Anthrafuchsone reacted with methylmagnesium iodide in only the 1,2 manner (38); however, naphthofuchsone (LXX) underwent 1,6-addition with this re-

agent. The structure of the adduct (LXXI) was proved by a coupling reaction with the same reagent. This work is an extension of a similar series of experiments
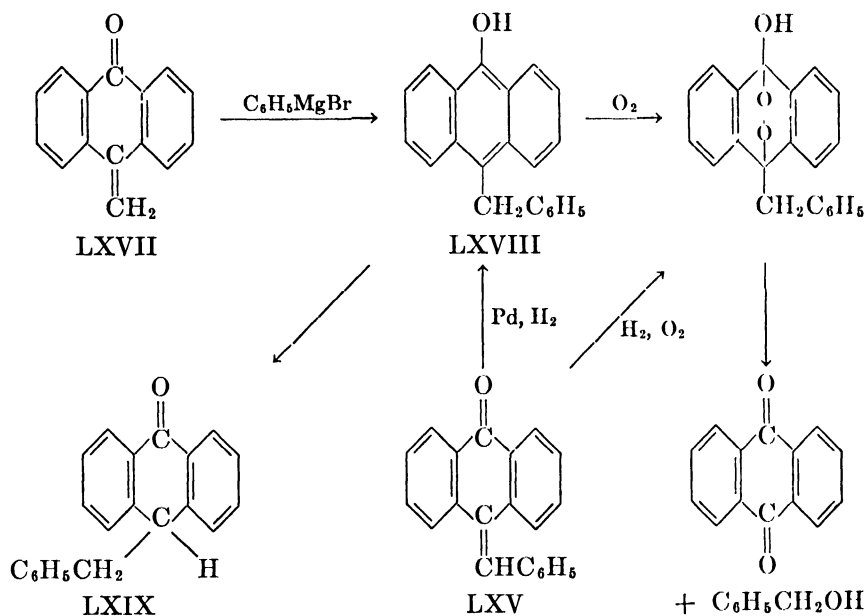
proving the nature of the product (LXXIII) of the reaction of fuchsone (LXXII) itself with the methyl Grignard reagent. Baeyer and Villiger (5) originally pro-

posed this course for the reaction in 1903, and Julian and Gist (38) were led to carry out a proof of structure analogous to that shown above. It may be pointed out that in this example and that of naphthofuchsone a benzenoid ring is generated by a process of 1,6-addition, while in the case of anthrafuchsone conjugate
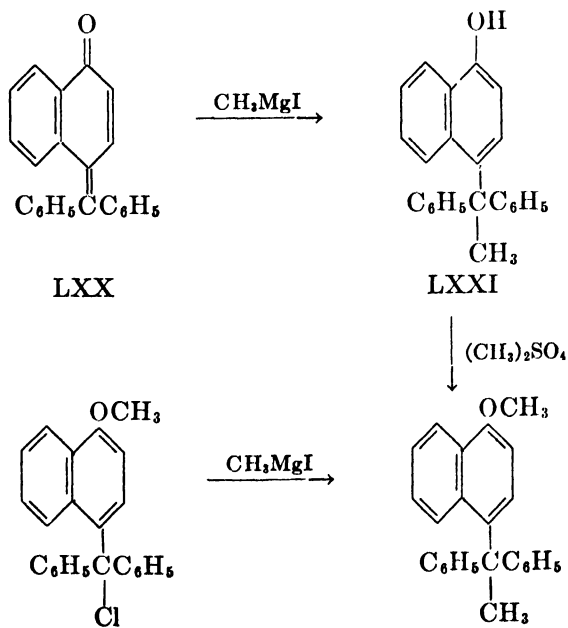
LXXII   LXXIII
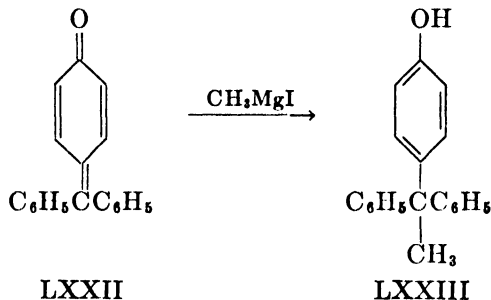
reaction could not form an additional aromatic system.

2. To hindered diaryl ketones

That 1,6-addition of Grignard reagents occurs with much simpler diaryl ketones has been shown by Fuson and coworkers. By taking advantage of the hindering effect of the duryl (2,3,5,6-tetramethylphenyl, abbreviated as Dur) radical to prevent 1,2-addition, Fuson and McKusick (23) observed conjugate reaction of the benzyl and t-butyl Grignard reagents with duryl phenyl ketone (LXXIV). These and related transformations are illustrated in the diagram.
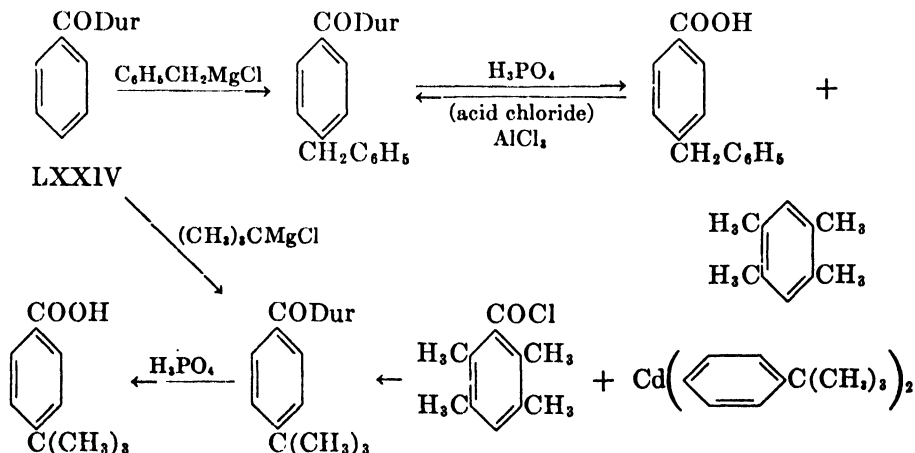
A similar reaction occurred with duryl 2-(o-methoxyphenyl)phenyl ketone (LXXV) (19). Later work (28) has shown that the isopropyl, cyclohexyl, and s-butyl reagents also react in this manner with duryl phenyl ketone, and that reaction of duryl o-tolyl and 2,6-dimethylphenyl duryl ketones with t-butyl-magnesium chloride results in t-butylation in the 4 position with low yields.

In only one case has it been possible by extensive and exhaustive investigation

of the reaction mixture to prove the occurrence of simultaneous 1,2- 1,4-, and 1,6-addition of a Grignard reagent (24). Duryl phenyl ketone reacted with

$$
\text{LXXV} \xrightarrow{\ C_6H_5CH_2MgCl\ }
$$
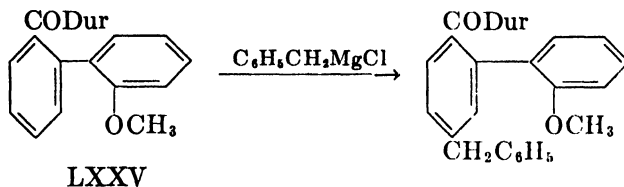
methylmagnesium iodide to give principally two isomeric dihydro products (LXXVI) of 1,4-addition, but small amounts of compounds reulting from the other modes of reaction were also iolated. The carbinol to be expected from 1,2-addition was not obtained but two dehydration products, 1-duryl-1-phenyl-

$$
\xrightarrow{\ CH_3MgI\ }\ \underbrace{A + B}_{LXXVI}\ +\ \underset{\underset{C_6H_5}{|}}{\overset{\overset{Dur}{|}}{C}}=CH_2\ +\ \underset{\underset{C_6H_5}{|}}{\overset{\overset{Dur}{|}}{(CH_2)_2O}}\ +\ \text{LXXIX}
$$

LXXVII   LXXVIII   LXXIX

AlCl₃ / durene

Pd–C

O₃
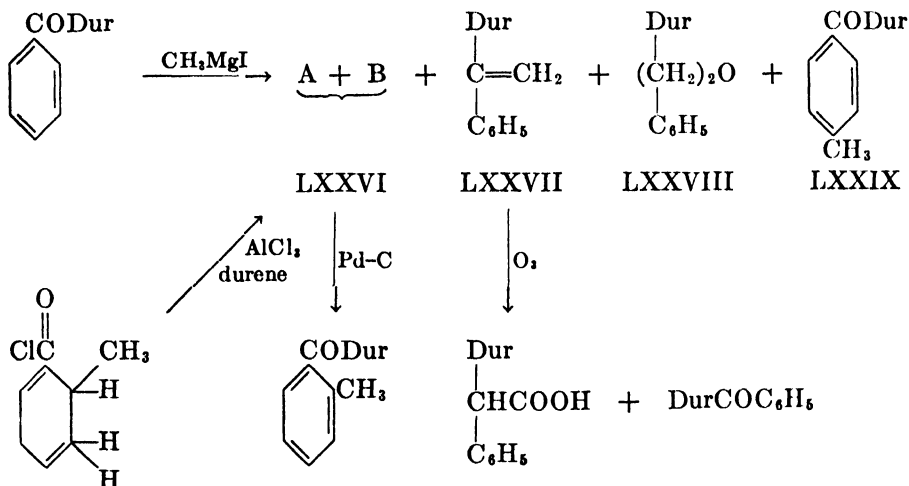
ethylene (LXXVII) and 2,3,5,6-tetramethylbenzohydryl ether (LXXVIII), were found. 1,6-Addition produced small amounts of duryl *p*-tolyl ketone (LXXIX). As indicated, one of the 1,4-adducts (A) was shown to be duryl 2,3-dihydro-*o*-tolyl ketone by synthesis from the corresponding acid chloride. Ozonolysis of LXXVII yielded both duryl phenyl ketone and durylphenylacetic acid.

Other examples of 1,6-addition will be mentioned in the following section, since they are of interest in connection with the replacement of groups by the action of the Grignard reagent.

C. MECHANISM OF CONJUGATE ADDITION

A discussion of the mechanism of the reactions which have been described must include an adaptation of well-known, previously expressed ideas concerning open systems, modern concepts of resonance, and the theory of nucleophilic attack. The Grignard reagent, or for that matter any organometallic compound, may be considered as containing a potential carbanion, and its reaction as involving

primarily attack of this negative radical upon a positive center. In the case of conjugated systems this center may be transferred from, for example, the carbonyl carbon atom to the last atom in the system. We may represent this action by the following extreme resonance structure (LXXX), where the hindered ketones are chosen as an example:


LXXX
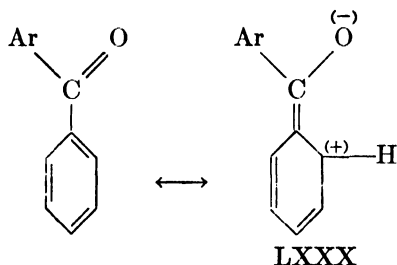
It is reasonable to assume, then, that the more positive magnesium atom of the reagent will coördinate with the negative oxygen atom and the negative carbanion will be attracted by the positive center shown above. This transition complex then reacts as indicated, with the transfer of the Grignard radical with its pair of electrons to the carbon atom in the nucleus to generate the halomagnesium enolate (LXXXI). Hydrolysis would then produce the enol (LXXXII) itself, which may ketonize to give the dihydro aromatic ketone (LXXXIII), the product usually isolated in many cases which have been mentioned. That the enol may be stable is demonstrated by those examples in which the enol peroxide
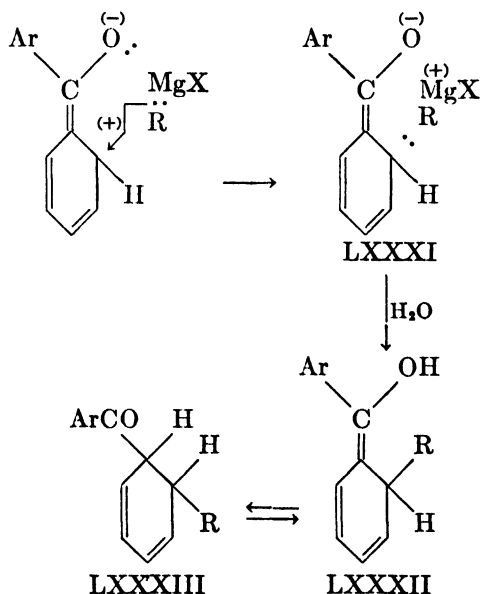
was obtained. However, the majority of products isolated from these reaction mixtures are fully aromatic, and the mechanism of elimination of hydrogen is

obscure. Several explanations might be advanced. Disproportionation of the dihydro compound would aromatize two-thirds of the material and saturate one-third. The saturated compound would be capable of existence in stereoisomeric
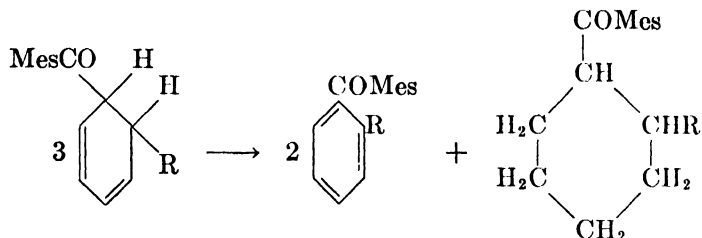
forms and this might account for the formation of the gums usually observed. The fact that a yield of aromatic material greater than 67 per cent has never been claimed is also in agreement with this mechanism. Elimination of hydride ions seems unlikely. A third course is the air oxidation of the mixture before or after hydrolysis. Probably either the first or the third explanation is near the truth.

Of course, it is realized that the mechanism proposed above, involving cyclization, cannot be applied unmodified in the case of 1,6-addition, and the reason for the tendency of certain reagents, notably benzyl, to react in this manner is again obscure. The same type of extreme polarized structure may again be suggested:
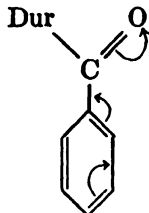
Other considerations are similar, except that no dihydroaromatic compound of this nature has ever been isolated.

III. REPLACEMENT OF FUNCTIONAL GROUPS

The preceding section has been concerned with the replacement by the radical of an organometallic reagent of hydrogen on an aromatic ring, or in some cases the formation of dihydroaromatic compounds by conjugate addition. This type of reaction has also been observed to result in the replacement of two substituents, —the methoxyl group and, in one case, a bromine atom.

A. THE METHOXYL GROUP

1. "Unactivated" methoxyl groups

In only two cases has it been claimed that an organometallic compound was capable of replacing a methoxyl group which was not ortho or para to some electron-attracting or activating group. In 1914 Späth (49) stated that he isolated what was probably isoamylbenzene from the reaction of anisole with isoamyl-
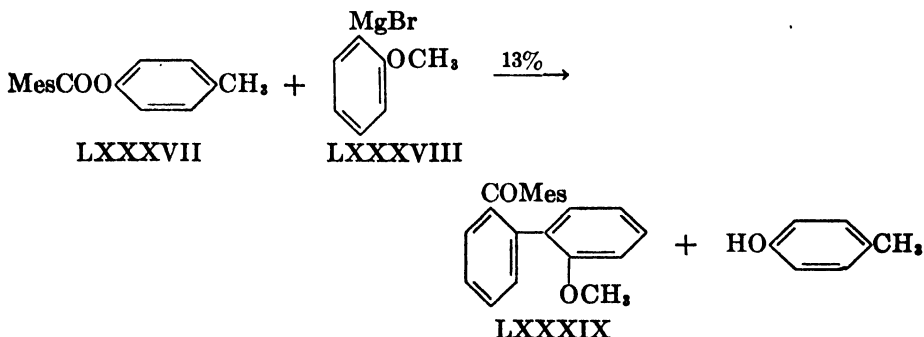
magnesium iodide. However, the principal product was phenol and no substantiating evidence was advanced for the identity of the supposed hydrocarbon, isolated in very small amount. Although the yield was again almost negligible, the work of Price and Meuller (46) was more convincing. These authors treated *p*-methoxyphenylmagnesium bromide (LXXXIV) with 1,2-dibromocyclohexane and isolated two minor products, 4,4'-dimethoxybiphenyl (LXXXV) and 4,4''-dimethoxy-*p*-terphenyl (LXXXVI).

LXXXIV   LXXXV   LXXXVI
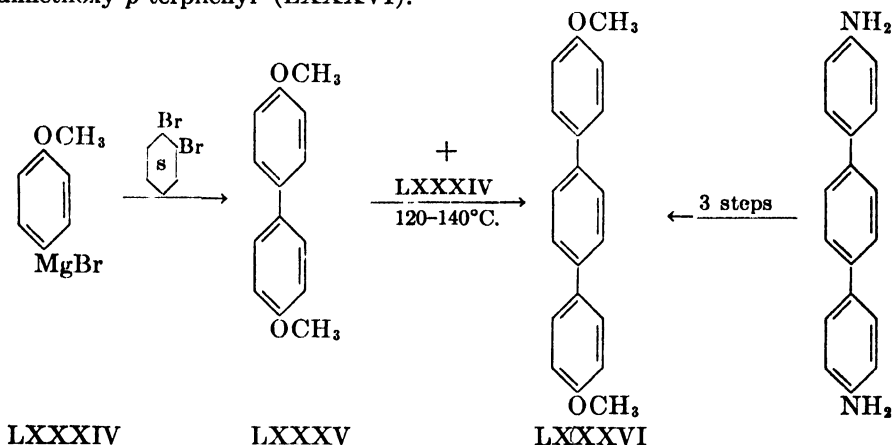
Treatment of LXXXIV with LXXXV also yielded LXXVI. The terphenyl was finally prepared from the corresponding diamine by successive tetrazotization, hydrolysis, and methylation. This extraordinary example is apparently the only one of its type which has been thoroughly investigated.

2. Methoxyl groups activated by an ortho substituent

(a) *The hindered carbonyl group:* As previously discussed, the reaction of aryl mesitoates with Grignard reagents led to conjugate addition (17). However, the presence of an ortho methoxyl group in the reagent resulted in a new reaction, the replacement of the substituent. Thus *p*-cresyl mesitoate (LXXXVII) and *o*-methoxyphenylmagnesium bromide (LXXXVIII) reacted to give mesityl 2-(*o*-
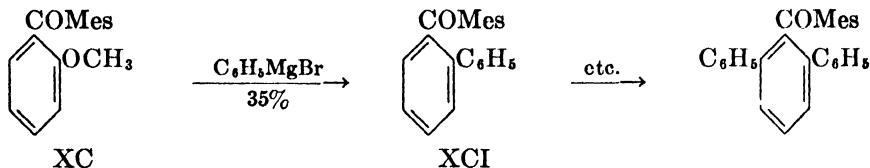

methoxyphenyl)phenyl ketone (LXXXIX).

A similar observation was that duroyl chloride, upon treatment with the same reagent, yielded the duryl analog of LXXXIX (19).

$$COCl\;(H_3C,CH_3,H_3C,CH_3\text{-benzene}) + MgBr\;(\text{-benzene-}OCH_3) \longrightarrow CODur\;(\text{-benzene-}OCH_3)$$
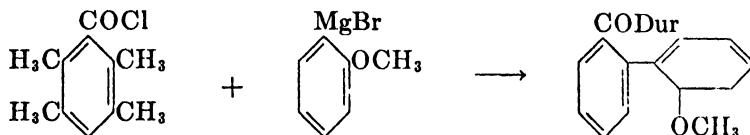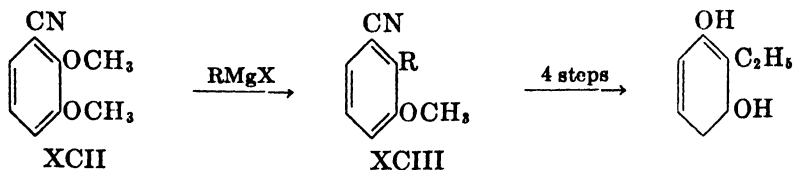
Logically, these observations led to the investigation of the methoxyaryl ketones, presumed intermediates, and it was soon discovered by Fuson and Speck (27) and others that arylation was facilitated, proceeding in better yield and under milder conditions, if it were possible for the reaction to result in the replacement of a methoxyl group ortho to the carbonyl group. As an example we compare the reactions of mesityl phenyl ketone and mesityl o-methoxyphenyl ketone (XC) with phenylmagnesium bromide. As previously stated, the former arylates in the ortho position in 18 per cent yield, while the latter undergoes replacement of the substituent to give the same product in 35 per cent yield. As in

$$\underset{XC}{COMes\;(\text{-benzene-}OCH_3)} \xrightarrow[35\%]{C_6H_5MgBr} \underset{XCI}{COMes\;(\text{-benzene-}C_6H_5)} \xrightarrow{\text{etc.}} COMes\;(C_6H_5\text{-benzene-}C_6H_5)$$

several other cases, this compound may be arylated further by the same reagent. The product of replacement may be isolated under mild conditions; thus it appears that replacement proceeds preferentially. Table 1 includes the known examples of this type of reaction. The higher yields in the examples involving the naphthalene derivative were interpreted as being another indication of the greater double-bond character between the 1 and 2 positions of that nucleus. As would be predicted on the basis of a mechanism involving conjugate addition, methoxyl groups in the meta position were unaffected, conjugate addition proceeding normally (Section III, A, 3, b).

(b) *The cyano group:* In the above reactions advantage was taken of the hindering effect of either the mesityl or the duryl radical to prevent normal 1,2-addition. That this was unnecessary was shown by Richtzenhain (47), who found that

$$\underset{XCII}{CN\;(\text{-benzene-}OCH_3,OCH_3)} \xrightarrow{RMgX} \underset{XCIII}{CN\;(\text{-benzene-}R,OCH_3)} \xrightarrow{4\text{ steps}} OH\;(\text{-benzene-}C_2H_5,OH)$$

R = C_2H_5 (60%); i-C_3H_7 (81%, or 83% (21)); n-C_4H_9 (80%); i-C_4H_9 (45%); n-C_7H_{15} (62%); cyclo-C_6H_{11} (68%); C_6H_5 (31%).

activation by the sluggish cyano grouping, combined with flanking by a second methoxyl group, also permitted replacement of the ortho methoxyl group 2,3-Dimethoxybenzonitrile (XCII) reacted with Grignard reagents to yield

2-substituted compounds (XCIII) (47, 48). The structure of the ethyl derivative
was proved by successive hydrolysis to the amide, degradation to the amine,
diazotization, and hydrolysis to 2-ethylresorcinol. The corresponding 2-allyloxy-
and 2-benzyloxy- compounds gave the same product (XCIII) with ethylmag-
nesium bromide but in much lower yield (47); but no replacement was observed
with the 2-acetate or with a free hydroxyl group in this position. Strangely
enough, methylmagnesium iodide reacted only in the normal manner. In investi-
gating this reaction further, Fuson, Gaertner, and Chadwick (21) found that
more than a slight excess of reagent is to be avoided, since under these conditions
the product of *both* replacement and 1,2-addition is the major one. Steric hin-
drance in the reagent prevents replacement, *t*-butylmagnesium chloride adding
exclusively in the 1,2 manner. These authors also found that two substituted

TABLE 1

| KETONE	R OF RMgX	POSITION OF ENTERING GROUP(S)	YIELD	REFERENCES
			per cent	
2-CH₃OC₆H₄COMes*............	o-CH₃OC₆H₄	2	47	(27)
	Phenyl	2; 2,6	35; 20	(27)
	Phenyl	2	59	(27)
	1-Naphthyl	2	76	(27)
2-CH₃OC₁₀H₆COMes...........	Methyl	2	56	(27)
	Ethyl	2	80	(27)
	n-Butyl	2	55	(27)
2-CH₃O-5-CH₃C₆H₃COMes.......	Ethyl	2	28	(27)
	Phenyl	2; 2,6	18; 20	(27)
2,3-(CH₃O)₂C₆H₃COMes.........	Benzyl	2	7	(19)
2,6-(CH₃O)₂C₆H₃CODur†	Methyl	2,6	47	(28)

*Mes = 2,4,6-triphenyl.
†Dur = 2,3,5,6-tetramethylphenyl.

2,3-dimethoxybenzonitriles, one bearing a methyl group in position 5 (XCIV)
and a bromo derivative of uncertain structure substituted in either the 6 or the
4 position (XCV), also underwent replacement of the ortho methoxyl group with
the ethyl reagent. Still other 2,3-dimethoxybenzonitriles which have been shown
by Richtzenhain and Nippus (48a) to undergo replacement of the ortho meth-
oxyl group with the ethyl reagent are: 2,3-dimethoxy-5-propylbenzonitrile (20
per cent, impure); 4,5-dimethoxyisophthalonitrile (75 per cent); and 2,3,4-
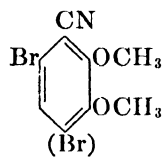trimethoxybenzonitrile (45 per cent).

These authors reported that the following related compounds reacted nor-
mally with Grignard reagents: 2-methoxy-3-methylbenzonitrile, 3-chloro-2-meth-
oxybenzonitrile, 1-methoxy-2-naphthonitrile, 2,3-dimethoxybenzalaniline,
o-isoeugenol methyl ether, 2,3-dimethoxybenzophenone, and ethyl 2,3-dimeth-
oxybenzoate. 3-Iodo-2-methoxybenzonitrile underwent a Grignard exchange re-
action to give, on hydrolysis, 2-methoxybenzonitrile. Under the usual conditions

β-(2,3-dimethoxyphenyl)acrylonitrile   and   6,7-dimethoxy-1-(2,3-dimethoxy-phenyl)isoquinoline gave unidentified products and 4-chloro-3-methoxy-2-naph-thonitrile and the 4-bromo analog did not react with Grignard reagents.

Attempts (18, 21) to replace methoxyl groups in related compounds not hav-ing the 2,3-dimethoxy grouping met with failure, only normal addition being de-tected; these will be discussed later in connection with the mechanism of this reaction.
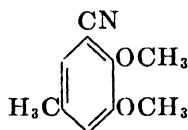

XCIV   XCV

Later, Richtzenhain and Miedrach (47a) adapted the reaction to the prepara-tion of 2-naphthyl-3-methoxybenzonitriles. Unfortunately, when naphthyl re-agents themselves were used, the yields of replacement products were low (α-, 6.5 per cent; β-, 7 per cent). However, when the reagent from 2-bromo-3,4-dihydronaphthalene was used, the yield of aromatized replacement product, obtained directly, was 26 per cent. 2-Chloro-1,2,3,4-tetrahydronaphthalene led to the corresponding tetrahydro derivative in 55 per cent yield.

3. Methoxyl groups activated by a para substituent

(a) The cyano group: Only one example of this reaction has been described in the literature. Haller and Schaffer (33) treated 3,4,5-trimethoxybenzonitrile (XCVI) with isobutylmagnesium iodide in refluxing toluene and isolated, in
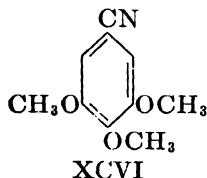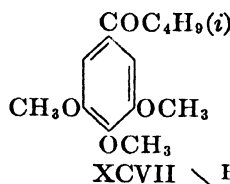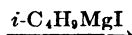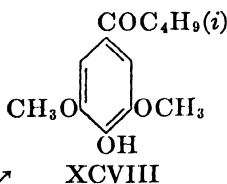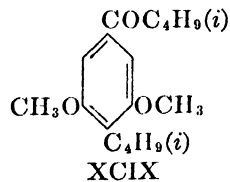
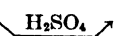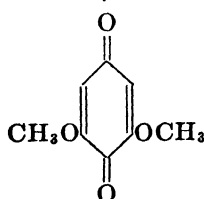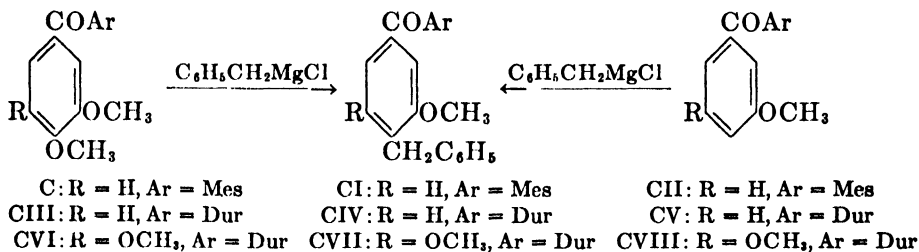addition to the normal product (XCVII), two other ketones. That obtained in the larger amount was phenolic in nature, the assigned structure being XCVIII. This formula was later confirmed by Hurd and Winberg (35) by oxidation of the compound to 2,6-dimethoxyquinone; they also obtained the phenolic ketone (XCVIII) by the action of sulfuric acid on XCVII. The other abnormal product was presumably 3,5-dimethoxy-4-isobutylphenyl isobutyl ketone (XCIX). The latter authors believed that its formation proceeded through an abnormal ether cleavage, since only the normal product was obtained at 40°C. and pyrogallol trimethyl ether was cleaved to 1,3-pyrogallol dimethyl ether by methylmagnesium iodide at 110°C. 3,4,5-Trimethoxybenzonitrile also undergoes replacement of the para group to give 3,5-dimethoxy-4-ethylpropiophenone (22 per cent yield) when treated with ethylmagnesium bromide (48a). 3,4-Dimethoxybenzonitrile and piperononitrile react normally with Grignard reagents (21).

(b) *The hindered carbonyl group:* Although, in view of the ease of replacement of methoxyl groups ortho to hindered carbonyl groups, it was early attempted to replace similarly such groups in the para position, only dihydro compounds of uncertain structure have been obtained from duryl *p*-methoxyphenyl ketone and the mesityl analog with the benzyl Grignard reagent (19). However, the previously cited examples of replacement of ortho methoxyl groups, which appeared to be promoted by the presence of a flanking methoxyl in the meta position, led Fuson and Gaertner (19) to investigate the action of the benzyl reagent on 3,4-dimethoxyphenyl mesityl ketone (C). As hoped, the expected product (CI) of replacement was obtained, the yield being 22 per cent. The

COAr   COAr   COAr

R⟩OCH₃ —C₆H₅CH₂MgCl→ R⟩OCH₃ ←C₆H₅CH₂MgCl— R⟩OCH₃
  OCH₃   CH₂C₆H₅

C: R = H, Ar = Mes   CI: R = H, Ar = Mes   CII: R = H, Ar = Mes
CIII: R = H, Ar = Dur   CIV: R = H, Ar = Dur   CV: R = H, Ar = Dur
CVI: R = OCH₃, Ar = Dur   CVII: R = OCH₃, Ar = Dur CVIII: R = OCH₃, Ar = Dur

structure was proved by the 1,6-addition of benzylmagnesium chloride to mesityl *m*-methoxyphenyl ketone (CII). The series of reactions was extended to the duryl analogs (CIII, CIV, and CV) and to duryl 3,4,5-trimethoxyphenyl ketone (CVI) in 42 per cent and 58 per cent yields, respectively, for the replacements. The comparatively high yield in the last case suggests that the promoting effect of the flanking methoxyl group on the replacement reaction was additive. Treatment of C with phenylmagnesium bromide, followed by bromination, gave a compound having the composition of a monobromo derivative of the corresponding replacement product. Duryl 3,4-methylenedioxyphenyl ketone did not undergo cleavage of the methylenedioxy ring (19).

B. A BROMO SUBSTITUENT

A single report of the replacement of a bromine atom ortho to a hindered carbonyl group exists. Fuson and Speck (27) treated *o*-bromophenyl mesityl

ketone (CIX) with phenylmagnesium bromide and observed the formation of 2,6-diphenylphenyl mesityl ketone (CX) as a result of both replacement and 1,4-addition.

COMes   COMes

$C_6H_5MgBr \longrightarrow$

CIX   CX
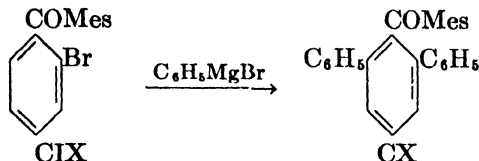
C. MECHANISM OF REPLACEMENT

Since a mechanism of simple ether cleavage appears untenable, it seems that most of the same considerations which were mentioned in connection with the mechanism of conjugate addition apply to the replacement of substituents by the organometallic compounds. Again considering the Grignard reagent as containing a potential carbanion, the replacement might proceed through nucleophilic attack of this ion on the positive center generated by resonance involving the activating group and a double bond in the aromatic nucleus. The extreme structure shown probably should be postulated as being generated at the instant of the attack and at the demand of the attacking reagent. It seems probable that this reaction involves the cyclic intermediate indicated; a six-membered ring is formed by supposing that the reagent coördinates between the oxygen atoms. There have been references (27, 47) to hydrolysis, followed by "elimination of the elements of methanol"; however, the fact that the simultaneous replace-

COMes

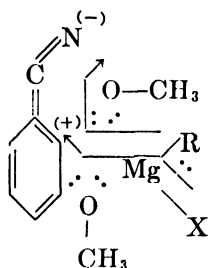$\longrightarrow$ R $+ \quad OCH_3^- + \overset{+}{M}gX$
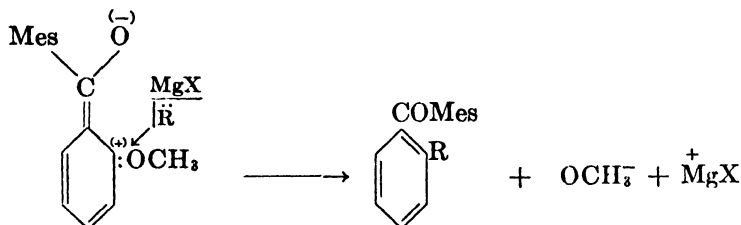
ment of two methoxyl groups without isolation of the mono-replacement product has been observed (page 515) seems to eliminate this possibility. This reaction must surely involve regeneration of the activating group before the second replacement can occur.

This mechanism alone, however, seems inadequate to explain the failure of the following nitriles to undergo replacement (18, 21).

CN   CN   CN
   OCH₃   OCH₃   CH₃O   OCH₃

CN   CN   CN
   OCH₃   O   CH₂   O
CH₃O   O   CH₂   CH₂
   O
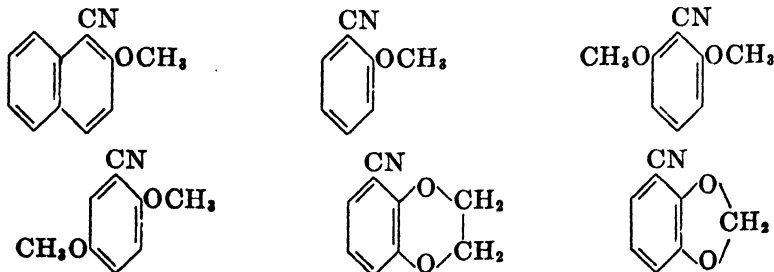
Of course, it may be argued that in these cases the reactivity of the cyano grouping merely predominated, but there must be some explanation for the promoting effect of the flanking group in the 2,3-dimethoxyben.''nitriles. A quite attractive rationalization involves coördination of the reagent between the two methoxyl groups so as to provide some necessary orientation for t!:) attack of the radical. It seems possible that the electron-attracting power of the second meth-

oxyl group may also play a part in increasing the positive nature of the attacked ortho carbon atom. Of course, it is to be remembered that R and X are thought to be in a perpendicular plane, one above the plane of the paper and the other below. Again a five-membered ring is suggested for the transition stage.

In the case of replacement of a para methoxyl group, a similar reactive complex may be formulated. Apparently the promoting effect of this sort of system is sufficiently great to make the difference between success and failure of the replacement. It is also interesting that no compound bearing both the radical of a
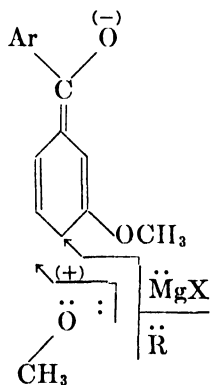
Grignard reagent and a methoxyl group on the same carbon atom has ever been shown to exist.

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